

ORGANIC COMPOUND COATED STEEL SHEET EXCELLENT IN CORROSION RESISTANCE

Publication number: JP2001335955

Publication date: 2001-12-07

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Classification:

- International: B05D3/10; B05D7/14; B05D7/24; B32B15/08;
B32B15/18; B32B27/38; C09D5/08; C09D163/00;
C09D201/00; C23C22/07; C23C22/40; C23C22/42;
C23C26/00; C23C28/00; C23F11/00; B05D3/10;
B05D7/14; B05D7/24; B32B15/08; B32B15/18;
B32B27/38; C09D5/08; C09D163/00; C09D201/00;
C23C22/05; C23C26/00; C23C28/00; C23F11/00;
(IPC1-7): C23C22/07; B05D3/10; B05D7/14; B05D7/24;
B32B15/08; B32B15/18; B32B27/38; C09D5/08;
C09D163/00; C09D201/00; C23C22/40; C23C22/42;
C23C26/00; C23C28/00; C23F11/00

- European:

Application number: JP20000161050 20000530

Priority number(s): JP20000161050 20000530

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Abstract of JP2001335955

PROBLEM TO BE SOLVED: To provide an organic compound coated steel sheet safe and harmless to a person in the production and also utilization, and excellent in corrosion resistance. SOLUTION: The surface of a galvanized steel sheet or an aluminum-based plated steel sheet is provided with an organic film containing any rust preventive addition component (B) selected from (a) Ca ion-exchanged silica and phosphate, (b) Ca ion-exchanged silica, phosphate and silicon oxide, (c) a calcium compound and silicon oxide, (d) a calcium compound, phosphate and silicon oxide, (e) molybdate, (f) one or more kinds of organic compounds selected from triazoles, thiols, triadiazoles, triazoles and thiurams by 1 to 100 pts.wt. in total (solid content) to 100 pts.wt. (solid content) of a film forming organic resin (A).

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文献 4

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2001-335955

(P2001-335955A)

(43) 公開日 平成13年12月7日 (2001.12.7)

(51) Int.Cl. ⁷	識別記号	F I	キーワード (参考)
C 2 3 C 22/07		C 2 3 C 22/07	4 D 0 7 5
B 0 5 D 3/10		B 0 5 D 3/10	L 4 F 1 0 0
7/14		7/14	A 4 J 0 3 8
7/24	3 0 2	7/24	3 0 2 E 4 K 0 2 6
	3 0 3		3 0 3 B 4 K 0 4 4
審査請求 未請求 請求項の数18 O L (全 27 頁) 最終頁に続く			

(21) 出願番号 特願2000-161050 (P2000-161050)

(22) 出願日 平成12年5月30日 (2000.5.30)

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(54) 【発明の名称】 耐食性に優れた有機被覆鋼板

(57) 【要約】

【課題】 製造工程や使用する際にも安全、無害であって、しかも優れた耐食性が得られる有機被覆鋼板を提供する。

【解決手段】 亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面に、皮膜形成有機樹脂 (A) 100重量部 (固形分) に対して、(a) Caイオン交換シリカ及びリン酸塩、(b) Caイオン交換シリカ、リン酸塩及び酸化ケイ素、(c) カルシウム化合物及び酸化ケイ素、(d) カルシウム化合物、リン酸塩及び酸化ケイ素、(e) モリブデン酸塩、(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、のうちのいずれかの防錆添加成分 (B) を合計で1~100重量部 (固形分) 含有する有機皮膜を有することを特徴とする。

【請求項10】 皮膜形成有機樹脂(A)がOH基及び／又はCOOH基を有する有機高分子樹脂であることを特徴とする請求項1、2、3、4、5、6、7、8又は9に記載の耐食性に優れた有機被覆鋼板。

【請求項11】 有機高分子樹脂が熱硬化性樹脂であることを特徴とする請求項10に記載の耐食性に優れた有機被覆鋼板。

【請求項12】 熱硬化性樹脂がエポキシ樹脂及び／又は変性エポキシ樹脂であることを特徴とする請求項11に記載の耐食性に優れた有機被覆鋼板。

【請求項13】 亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面に、6価クロムを含まない化成処理皮膜を有し、その上層に有機皮膜を有することを特徴とする請求項1、2、3、4、5、6、7、8、9、10、11又は12に記載の耐食性に優れた有機被覆鋼板。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、自動車、家電、建材用途などに最適な有機被覆鋼板に関し、製品を取扱う作業やユーザーへの影響、製造時の排水処理対策、さらには使用環境下における製品からの有害物質の揮発・溶出などの環境問題に適應するために、製造時及び製品中に環境・人体に有害なクロム、鉛、カドミウム、水銀などの重金属を全く含まない環境適応型表面処理鋼板に関するものである。

【0002】

【従来の技術】家電製品用鋼板、建材用鋼板、自動車用鋼板には、従来から亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面に、耐食性(耐白錆性、耐赤錆性)を向上させる目的で、クロム酸、重クロム酸又はその塩類を主要成分とした処理液によるクロメート処理が施された鋼板が幅広く用いられている。このクロメート処理は耐食性に優れ、且つ比較的簡単に行うことができる経済的な処理方法である。

【0003】クロメート処理は公害規制物質である6価クロムを使用するものであるが、この6価クロムは処理工程においてクロースドシステムで処理され、完全に還元・回収されて自然界には放出されていないこと、また、有機皮膜によるシーリング作用によってクロメート皮膜中からのクロム溶出もほぼゼロにできることから、実質的には6価クロムによって環境や人体が汚染されることはない。しかしながら、最近の地球環境問題から、6価クロムを含めた重金属の使用を自主的に削減しようとする動きが高まりつつある。また、廃棄物のシュレッターダストを投棄した場合に環境を汚染しないようにするため、製品中にできるだけ重金属を含ませない若しくはこれを削減しようとする動きも始まっている。

【0004】このようなことから、亜鉛系めっき鋼板の白錆の発生を防止するために、クロメート処理によらない無公害な処理技術、所謂クロムフリー技術が数多く提

案されている。このうち有機系化合物や有機樹脂を利用した方法もいくつか提案されており、例えば、以下のような方法を挙げることができる。

【0005】(1) タンニン酸を用いる方法(例えば、特開昭51-71233号)

(2) エポキシ樹脂とアミノ樹脂とタンニン酸を混合した熱硬化性塗料を用いる方法(例えば、特開昭63-90581号)

(3) 水系樹脂と多価フェノールカルボン酸の混合組成物を用いる方法(例えば、特開平8-325760号)などのようなタンニン酸のキレート力を利用する方法

【0006】(4) ヒドラジン誘導体水溶液をブリキ又は亜鉛鉄板の表面に塗布する表面処理方法(例えば、特公昭53-27694号、特公昭56-10386号)

(5) アシルザルコシンとベンゾトリアゾールとの混合物にアミンを付加させて得られたアミン付加塩を含む防錆剤を用いる方法(例えば、特開昭58-130284号)

(6) ベンゾチアゾール化合物などの複素環化合物とタンニン酸を混合した処理剤を用いる方法(例えば、特開昭57-198267号)

【0007】

【発明が解決しようとする課題】しかしながら、これらの従来技術には以下に述べるような問題点がある。まず、上記(1)～(4)の方法はいずれも耐食性の面で問題がある。これは、いずれの方法によっても、得られる皮膜が自己補修効果を有していないことに一因がある。すなわち、クロメート皮膜では、

(a) バリア効果：3価Cr主体の難溶性化合物(水和酸化物)による腐食因子(水、酸素、塩素など)に対する障壁効果

(b) 自己補修効果：6価Crによる腐食起点での保護皮膜形成効果

の両者の相乗効果によって高度の耐食性を発現する。ところが、従来のクロムフリー技術では、バリア効果についてはクロムに頼らなくとも有機樹脂などによってある程度付与できるが、自己補修効果については、6価Crの代替となる自己補修性発現物質が提供されていなかったため、高度の耐食性は実現できなかった。

【0008】また、上記(1)の方法では耐食性が不十分であるだけでなく、処理後の均一な外観が得られない。また、上記(2)の方法は、特に亜鉛系又はアルミニウム系めっき表面に直接、薄膜状(0.1～5μm)の防錆皮膜を形成することを狙いとしたものではなく、このため亜鉛系又はアルミニウム系めっき表面に薄膜状に適用したとしても十分な防食効果は得られない。また、上記(3)の方法についても同様に耐食性が不十分である。

【0009】さらに上記(4)の方法は亜鉛系又はアルミニウム系めっき鋼板について適用したものではなく、

(i) Caイオン交換シリカ
膜厚が0.1~5 μ mの有機皮膜を有することを特徴とする耐食性に優れた有機被覆鋼板。

【0018】[6] 亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面に、皮膜形成有機樹脂(A)100重量部(固形分)に対して下記(e)及び(f)の防錆添加成分(B)を合計で1~100重量部(固形分)含有する。

(e) モリブデン酸塩

(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物

膜厚が0.1~5 μ mの有機皮膜を有することを特徴とする耐食性に優れた有機被覆鋼板。

【0019】[7] 亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面に、皮膜形成有機樹脂(A)100重量部(固形分)に対して下記(e)、(f)、(g)及び(h)の防錆添加成分(B)を合計で1~100重量部(固形分)含有する、

(e) モリブデン酸塩

(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物

(g) カルシウム及び/又はカルシウム化合物

(h) リン酸塩及び/又は酸化ケイ素

膜厚が0.1~5 μ mの有機皮膜を有することを特徴とする耐食性に優れた有機被覆鋼板。

【0020】[8] 亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面に、皮膜形成有機樹脂(A)100重量部(固形分)に対して下記(e)、(f)及び(i)の防錆添加成分(B)を合計で1~100重量部(固形分)含有する、

(e) モリブデン酸塩

(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物

(i) Caイオン交換シリカ

膜厚が0.1~5 μ mの有機皮膜を有することを特徴とする耐食性に優れた有機被覆鋼板。

【0021】[9] 上記[1]~[8]のいずれかの有機被覆鋼板において、有機皮膜が、さらに固形潤滑剤

(C)を含み、該固形潤滑剤(C)の含有量が皮膜形成有機樹脂(A)100重量部(固形分)に対して1~80重量部(固形分)であることを特徴とする耐食性に優れた有機被覆鋼板。

[10] 上記[1]~[9]のいずれかの有機被覆鋼板において、皮膜形成有機樹脂(A)がOH基及び/又はCOOH基を有する有機高分子樹脂であることを特徴とする耐食性に優れた有機被覆鋼板。

【0022】[11] 上記[10]の有機被覆鋼板におい

て、有機高分子樹脂が熱硬化性樹脂であることを特徴とする耐食性に優れた有機被覆鋼板。

[12] 上記[11]の有機被覆鋼板において、熱硬化性樹脂がエポキシ樹脂及び/又は変性エポキシ樹脂であることを特徴とする耐食性に優れた有機被覆鋼板。

[13] 上記[1]~[12]のいずれかの有機被覆鋼板において、亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面に、6価クロムを含まない化成処理皮膜を有し、その上層に有機皮膜を有することを特徴とする耐食性に優れた有機被覆鋼板。

【0023】本発明の有機被覆鋼板の基本的な特徴は、亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面に、必要に応じて、6価クロムを含まない化成処理皮膜を形成した上で、皮膜形成有機樹脂(A)、好ましくはOH基及び/又はCOOH基を有する有機高分子樹脂

(さらに好ましくは熱硬化性樹脂、特に好ましくはエポキシ樹脂及び/又は変性エポキシ樹脂)に自己補修性発現物質(防錆添加成分)として、(a) Caイオン交換シリカ及びリン酸塩、(b) Caイオン交換シリカ、リン酸塩及び酸化ケイ素、(c) カルシウム化合物及び酸化ケイ素、(d) カルシウム化合物、リン酸塩及び酸化ケイ素、(e) モリブデン酸塩、(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、のうちのいずれか、若しくは上記(e)及び/又は(f)に他の成分を複合添加した防錆添加成分(B)を配合した有機皮膜を形成した点にある。

【0024】本発明では、上記のように有機皮膜中に、

(a) Caイオン交換シリカ及びリン酸塩

(b) Caイオン交換シリカ、リン酸塩及び酸化ケイ素

(c) カルシウム化合物及び酸化ケイ素

(d) カルシウム化合物、リン酸塩及び酸化ケイ素

(e) モリブデン酸塩

(f) トリアゾール類、チオール類、チアジアゾール

類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物

のうちのいずれかの、若しくは上記(e)及び/又は

(f)に他の成分を複合添加した防錆添加成分(B)

(自己補修性発現物質)を適量配合することにより、特に優れた耐食性能(自己修復効果)を得ることができる。このような有機皮膜中に上記(a)~(f)の成分を配合したことにより得られる防食機構は以下のように考えられる。

【0025】まず、上記(a)~(d)の成分は沈殿作用によって自己補修性を発現するもので、その反応機構は以下のステップで進むと考えられる。

【第1ステップ】：腐食環境下において、めっき金属である亜鉛やアルミニウムよりも率なカルシウムが優先溶解する。

【第2ステップ】：リン酸塩の場合、加水分解反応によ

いる場合には、黒変を防止する目的で電気めっき浴に鉄族金属イオン（Niイオン、Coイオン、Feイオン）を添加し、めっき皮膜中にこれらの金属を1ppm以上含有させておくことができる。この場合、めっき皮膜中の鉄族金属濃度の上限については特に制限はない。

【0034】亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面には、必要に応じてクロメート皮膜（6価クロムを含有する化成処理皮膜）以外の化成処理皮膜、すなわち6価クロムを含まない化成処理皮膜を形成することができる。この化成処理皮膜はめっき鋼板の活性度を抑制し、耐食性、密着性を向上する目的で形成されるもので、6価クロムを含有しない化成処理皮膜であればその種類に制限はない。

【0035】6価クロムを含有しない化成処理皮膜としては、例えば、

- (1) リン酸塩処理皮膜
 - (2) モリブデート又はタングステート処理皮膜、リン酸／モリブデン酸処理皮膜などの不動態化皮膜、
 - (3) 酸化リチウムなどのアルカリ金属酸化物と酸化ケイ素からなるアルカリシリケート処理皮膜
 - (4) 3価クロムからなる複合酸化物皮膜
 - (5) 酸化チタン、酸化ジルコニウムからなる酸化物皮膜
- などの無機系皮膜を適用することができる。

【0036】なお、上記(4)の3価クロムからなる複合酸化物皮膜としては、3価クロムの酸化物や水酸化物とシリカ、アルミナ、チタニア、ジルコニア、酸化亜鉛などの酸化物からなる複合酸化物皮膜などがそれに相当する。また、その製造方法については特に限定しないが、水溶性の3価クロム化合物を処理液として用いることが有効である。この水溶性の3価クロム化合物としては、水溶性のものであれば特に限定はなく、例えば、塩化クロム、硫酸クロム、酢酸クロム、ギ酸クロムなどが挙げられるが、特に酢酸クロムやギ酸クロムなどのカルボン酸クロムが好ましい。また、シリカ、アルミナ、チタニア、ジルコニア、酸化亜鉛などの酸化物としては、それら酸化物のコロイド及び／又は粉末を処理液に添加することが好ましい。

【0037】また、上記無機系皮膜以外に、例えば、

- (6) 有機系樹脂皮膜（膜厚0.1～2μm）又は有機複合シリケート皮膜
- (7) タンニン酸、フィチン酸、ホスホン酸などのキレート形成有機皮膜

(8) 上記(1)、(2)、(3)のいずれかの無機系皮膜中に有機樹脂を配合した複合皮膜などを適用することができる。上記のなかでも特に酸化ケイ素を含有する難溶性皮膜（例えば、アルカリシリケート皮膜など）が、亜鉛の白錆を抑制する観点から最も望ましい。

【0038】上記化成処理皮膜中には、皮膜の加工性、

耐食性を向上させることを目的として、さらに有機樹脂を配合することができる。この有機樹脂としては、エポキシ樹脂、ウレタン樹脂、アクリル樹脂、アクリルエチレン共重合体、アクリルステレン共重合体、アルキド樹脂、ポリエステル樹脂、エチレン樹脂などの1種又は2種以上を用いることができる。これらは水溶性樹脂及び／又は水分散性樹脂として皮膜中に導入できる。さらに、これらの水系樹脂に加えて、水溶性エポキシ樹脂、水溶性フェノール樹脂、水溶性ブタジエンラバー（SBR、NBR、MBR）、メラミン樹脂、ブロックイソシアネート、オキサゾリン化合物などを架橋剤として併用することが有効である。

【0039】上記化成処理皮膜中には、耐食性をさらに向上させるための添加剤として、さらに、ポリリン酸塩、リン酸塩（例えば、リン酸亜鉛、リン酸二水素アルミニウム、亜リン酸亜鉛など）、モリブデン酸塩、リンモリブデン酸塩（例えば、リンモリブデン酸アルミニウムなど）、有機リン酸及びその塩（例えば、フィチン酸、フィチン酸塩、ホスホン酸、ホスホン酸塩及びこれらの金属塩、アルカリ金属塩など）、有機インヒビター（例えば、ヒドラジン誘導体、チオール化合物、ジチオカルバミン酸塩など）、有機化合物（例えば、ポリエチレングリコールなど）などの1種又は2種以上を配合してもよい。

【0040】さらに、その他の添加剤として、有機着色顔料（例えば、縮合多環系有機顔料、フタロシアニン系有機顔料など）、着色染料（例えば、有機溶剤可溶性アゾ系染料、水溶性アゾ系金属染料など）、無機顔料（例えば、酸化チタンなど）、キレート剤（例えば、チオールなど）、導電性顔料（例えば、亜鉛、アルミニウム、ニッケルなどの金属粉末、リン化鉄、アンチモンドープ型酸化錫など）、カップリング剤（例えば、シランカップリング剤、チタンカップリング剤など）、メラミン・シアヌル酸付加物などの1種又は2種以上を添加することもできる。

【0041】また、上記化成処理皮膜中には、有機被覆鋼板の使用環境下での黒変（めっき表面の酸化現象の一種）を防止する目的で、鉄族金属イオン（Niイオン、Coイオン、Feイオン）の1種以上を添加してもよい。なかでもNiイオンの添加が最も好ましい。この場合、鉄族金属イオンの濃度としては、処理組成物中で1/100000M以上あれば所望の効果が得られる。鉄族イオン濃度の上限は特に定めないが、濃度の増加に伴い耐食性に影響を及ぼさない程度とするのが好ましい。これらの化成処理皮膜の膜厚は3μm以下とする。膜厚が3μmを超えると、加工性、導電性が低下するためである。下限は特に定めないが、耐食性向上効果が認められる膜厚とすればよい。

【0042】亜鉛系めっき鋼板又はアルミニウム系めっき鋼板の表面には、必要に応じて上記化成処理皮膜を形

加熱乾燥時にアルコキシシランの加水分解によるシラノール基の生成と樹脂粒子間のシラノール基の脱水縮合反応を利用した粒子間架橋を利用することができる。また、有機皮膜に使用する樹脂としては、有機樹脂をシランカップリング剤を介してシリカと複合化させた有機複合シリケートも好適である。

【0052】本発明では有機皮膜の耐食性や加工性の向上を担いとして、特に熱硬化性樹脂を用いることが望ましい。この場合、尿素樹脂（ブチル化尿素樹脂など）、メラミン樹脂（ブチル化メラミン樹脂）、ブチル化尿素・メラミン樹脂、ベンゾグアナミン樹脂などのアミノ樹脂、ブロックイソシアネート、オキサゾリン化合物、フェノール樹脂などの硬化剤を配合することができる。

【0053】以上述べた有機樹脂の中で、耐食性、加工性、塗装性を考慮すると、エポキシ樹脂、エチレン系樹脂が好ましく、特に、酵素などの腐食因子に対して優れた遮断性を有する熱硬化性のエポキシ樹脂や変性エポキシ樹脂が特に好適である。これらの熱硬化性樹脂としては、熱硬化性エポキシ樹脂、熱硬化性変性エポキシ樹脂、エポキシ基含有モノマーと共重合したアクリル系共重合体樹脂、エポキシ基を有するポリブタジエン樹脂、エポキシ基を有するポリウレタン樹脂、及びこれらの樹脂の付加物もしくは縮合物などが挙げられ、これらのエポキシ基含有樹脂の1種を単独で、または2種以上混合して用いることができる。

【0054】本発明では、有機皮膜中に自己補修性発現物質である下記(a)～(f)のうちのいずれかの防錆添加成分(B)、

- (a) Caイオン交換シリカ及びリン酸塩
- (b) Caイオン交換シリカ、リン酸塩及び酸化ケイ素
- (c) カルシウム化合物及び酸化ケイ素
- (d) カルシウム化合物、リン酸塩及び酸化ケイ素
- (e) モリブデン酸塩
- (f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物

若しくは上記(e)及び/又は(f)に他の成分を配合した防錆添加成分(B)を添加する。これら成分(a)～(f)による防食機構については先に述べた通りである。

【0055】上記成分(a)、(b)中に含まれるCaイオン交換シリカは、カルシウムイオンを多孔質シリカゲル粉末の表面に固定したもので、腐食環境下でCaイオンが放出されて沈殿膜を形成する。Caイオン交換シリカとしては任意のものを用いることができるが、平均粒子径が8μm以下、望ましくは4μm以下のものが好ましく、例えば、平均粒子径が2～4μmのものを用いることができる。Caイオン交換シリカの平均粒子径が6μmを超えると耐食性が低下するとともに、塗料組成物中での分散安定性が低下する。

【0056】Caイオン交換シリカ中のCa濃度は1wt%以上、望ましくは2～8wt%であることが好ましい。Ca濃度が1wt%未満ではCa放出による防錆効果が十分に得られない。なお、Caイオン交換シリカの表面積、pH、吸油量については特に限定されない。

【0057】以上のようなCaイオン交換シリカとしては、商品名でW.R.Grace&Co.製のSHIELDEX C303（平均粒子径2.5～3.5μm、Ca濃度3wt%）、SHIELDEX AC3（平均粒子径2.3～3.1μm、Ca濃度6wt%）、SHIELDEX AC5（平均粒子径3.8～5.2μm、Ca濃度6wt%）、富士シリシア化学(株)製のSHIELDEX（平均粒子径3μm、Ca濃度6～8wt%）、SHIELDEX SY710（平均粒子径2.2～2.5μm、Ca濃度6.6～7.5wt%）などを用いることができる。

【0058】上記成分(a)、(b)、(d)中に含まれるリン酸塩は、単塩、複塩などの全ての種類の塩を含む。また、それを構成する金属カチオンに限定はなく、リン酸亜鉛、リン酸マグネシウム、リン酸カルシウム、リン酸アルミニウムなどのいずれの金属カチオンでもよい。また、リン酸イオンの骨格や縮合度などにも限定はなく、正塩、二水素塩、一水素塩又は亜リン酸塩のいずれでもよく、さらに、正塩はオルトリン酸塩の他、ポリリン酸塩などの全ての縮合リン酸塩を含む。

【0059】上記成分(c)、(d)中に含まれるカルシウム化合物は、カルシウム酸化物、カルシウム水酸化物、カルシウム塩のいずれでもよく、これらの1種または2種以上を使用できる。また、カルシウム塩の種類にも特に制限はなく、ケイ酸カルシウム、炭酸カルシウム、リン酸カルシウムなどのようなカチオンとしてカルシウムのみを含む単塩のほか、リン酸カルシウム・亜鉛、リン酸カルシウム・マグネシウムなどのようなカルシウムとカルシウム以外のカチオンを含む複塩を使用してもよい。

【0060】上記成分(b)、(c)、(d)中に含まれる酸化ケイ素は、コロイダルシリカ、乾式シリカのいずれでもよい。コロイダルシリカとしては、水系皮膜形成樹脂をベースとする場合には、例えば、商品名で日産化学工業(株)製のスノーデックスO、スノーデックスN、スノーデックス20、スノーデックス30、スノーデックス40、スノーデックスC、スノーデックスS、触媒化成工業(株)製のカタロイドS、カタロイドSI-350、カタロイドSI-40、カタロイドSA、カタロイドSN、旭電化工業(株)製のアデライトAT-20～50、アデライトAT-20N、アデライトAT-300、アデライトAT-300S、アデライトAT-20Qなどを用いることができる。

【0061】また、溶剤系皮膜形成樹脂をベースとする場合には、例えば、商品名で日産化学工業(株)製のオ

ン酸イオン量が少なく、腐食起点を封鎖するだけの保護皮膜を形成できない。一方、(d1)/(d2)+(d3)が99/1を超えると、保護皮膜の形成にとって必要以上の量のカルシウムが溶出するばかりでなく、そのカルシウムと錯形成反応を起こすのに必要なリン酸イオンやカルシウムを吸着させるのに必要な酸化ケイ素が十分に供給されず、また、(d2)/(d3)が99/1を超えると溶出したカルシウムを吸着させるのに必要な酸化ケイ素が十分に供給されず、いずれの場合も耐食性が却って低下してしまう。

【0069】上記の防錆添加成分(a)～(f)は、先に述べたように腐食環境下において沈殿効果(成分(a)～(d)の場合)、不動化効果(成分(e)の場合)、吸着効果(成分(f)の場合)により、それぞれ保護皮膜を形成する。また、上記(a)～(d)、(e)、(f)の各成分によって得られる自己補修効果(上述した3つのタイプの保護皮膜形成効果)からして、より高度な自己補修性を得るには上記(e)及び/又は(f)に他の成分を複合添加した以下のような組み合わせの防錆添加成分(B)を調整(配合)するのが好ましく、特に、下記(6)及び(7)の場合に最も高度な自己補修性(すなわち、耐白錆性)が得られる。

【0070】(1) (e) モリブデン酸塩、(g) カルシウム及び/又はカルシウム化合物、及び(h) リン酸塩及び/又は酸化ケイ素、を配合した防錆添加成分

(2) (e) モリブデン酸塩、及び(i) Caイオン交換シリカ、を配合した防錆添加成分

(3) (f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、(g) カルシウム及び/又はカルシウム化合物、及び(h) リン酸塩及び/又は酸化ケイ素、を配合した防錆添加成分

【0071】(4) (f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、及び(i) Caイオン交換シリカ、を配合した防錆添加成分

(5) (e) モリブデン酸塩、及び(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、を配合した防錆添加成分

【0072】(6) (e) モリブデン酸塩、(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、(g) カルシウム及び/又はカルシウム化合物、及び(h) リン酸塩及び/又は酸化ケイ素、を配合した防錆添加成分

(7) (e) モリブデン酸塩、(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、及び(i)

Caイオン交換シリカ、を配合した防錆添加成分
ここで、適用し得るカルシウム化合物、リン酸塩、酸化ケイ素、Caイオン交換シリカについては、先に(a)～(d)の成分に関して述べたものと同様である。

【0073】上記(1)の(e) モリブデン酸塩、(g) カルシウム及び/又はカルシウム化合物、及び(h) リン酸塩及び/又は酸化ケイ素、を配合した防錆添加成分において、これら(e)、(g)及び(h)の配合比は固形分の重量比で(e)/(g)+(h)=1/99～99/1、好ましくは10/90～90/10、さらに好ましくは20/80～80/20が適当であり、また(g)/(h)=1/99～99/1、好ましくは10/90～90/10、さらに好ましくは20/80～80/20が適当である。

【0074】ここで、(e)/(g)+(h)が1/99未満又は99/1を超えては、異なる自己補修効果を複合させることによる効果が十分に得られない。また、(g)/(h)が1/99未満ではカルシウム溶出量が少なく、腐食起点を封鎖するだけの保護皮膜を形成できず、一方、99/1を超えると、保護皮膜の形成にとって必要以上の量のカルシウムが溶出するばかりでなく、そのカルシウムと錯形成反応を起こすのに必要なリン酸イオンやカルシウムを吸着させるのに必要な酸化ケイ素が十分に供給されないため、十分な自己補修効果が得られない。

【0075】上記(2)の(e) モリブデン酸塩及び(i) Caイオン交換シリカ、を配合した防錆添加成分において、(e)及び(i)の配合比は固形分の重量比で(e)/(i)=1/99～99/1、好ましくは10/90～90/10、さらに好ましくは20/80～80/20が適当である。ここで、(e)/(i)が1/99未満又は99/1を超えては、異なる自己補修効果を複合させることによる効果が十分に得られない。

【0076】上記(3)の(f) トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、(g) カルシウム及び/又はカルシウム化合物、及び(h) リン酸塩及び/又は酸化ケイ素、を配合した防錆添加成分において、これら(f)、(g)及び(h)の配合比は固形分の重量比で(f)/(g)+(h)=1/99～99/1、好ましくは10/90～90/10、さらに好ましくは20/80～80/20が適当であり、また、(g)/(h)=1/99～99/1、好ましくは10/90～90/10、さらに好ましくは20/80～80/20が適当である。

【0077】ここで、(f)/(g)+(h)が1/99未満又は99/1を超えては、異なる自己補修効果を複合させることによる効果が十分に得られない。また、(g)/(h)が1/99未満ではカルシウム溶出量が少なく、腐食起点を封鎖するだけの保護皮膜を形成でき

(1) ポリオレフィンワックス、パラフィンワックス：例えば、ポリエチレンワックス、合成パラフィン、天然パラフィン、マイクロワックス、塩素化炭化水素など

(2) フッ素樹脂微粒子：例えば、ポリフルオロエチレン樹脂（ポリ4フッ化エチレン樹脂など）、ポリフッ化ビニル樹脂、ポリフッ化ビニリデン樹脂など

【0086】また、この他にも、脂肪酸アミド系化合物（例えば、ステアリン酸アミド、パルミチン酸アミド、メチレンビスステアロアミド、エチレンビスステアロアミド、オレイン酸アミド、エシル酸アミド、アルキレン 10 ビス脂肪酸アミドなど）、金属石けん類（例えば、ステアリン酸カルシウム、ステアリン酸鉛、ラウリン酸カルシウム、パルミチン酸カルシウムなど）、金属硫化物（例えば、二硫化モリブデン、二硫化タングステンなど）、グラファイト、フッ化黒鉛、窒化ホウ素、ポリアルキレングリコール、アルカリ金属硫酸塩などの1種又は2種以上を用いてもよい。

【0087】以上の固形潤滑剤の中でも、特に、ポリエチレンワックス、フッ素樹脂微粒子（なかでも、ポリ4 20 フッ化エチレン樹脂微粒子）が好適である。ポリエチレンワックスとしては、例えば、ヘキスト社製のセリダスト 9615A、セリダスト 3715、セリダスト 3620、セリダスト 3910、三洋化成（株）製のサンワックス 131-P、サンワックス 161-P、三井石油化学（株）製のケミパール W-100、ケミパール W-200、ケミパール W-500、ケミパール W-800、ケミパール W-950などを用いることができる。

【0088】また、フッ素樹脂微粒子としては、テトラフルオロエチレン微粒子が最も好ましく、例えば、ダイキン工業（株）製のルプロン L-2、ルプロン L-5、三井・デュボン（株）製のMP1100、MP1200、旭アイシーアイフロポリマーズ（株）製のフルオンディスバージョン AD1、フルオンディスバージョン AD2、フルオン L141J、フルオン L150J、フルオン L155Jなどが好適である。また、これらのなかで、ポリオレフィンワックスとテトラフル 30 オロエチレン微粒子の併用により特に優れた潤滑効果が期待できる。

【0089】有機被膜中での固形潤滑剤（C）の配合量は、被膜形成有機樹脂（A）100重量部（固形分）に対して、1～80重量部（固形分）、好ましくは3～40重量部（固形分）とする。固形潤滑剤（C）の配合量が1重量部未満では潤滑効果が乏しく、一方、配合量が80重量部を超えると塗装性が低下するので好ましくない。

【0090】本発明の有機被膜鋼板が有する有機被膜は、通常、被膜形成有機樹脂（A）に自己補修性異現物質である、（a）Caイオン交換シリカ及びリン酸塩、（b）Caイオン交換シリカ、リン酸塩及び酸化ケイ 50

素、（c）カルシウム化合物及び酸化ケイ素、（d）カルシウム化合物、リン酸塩及び酸化ケイ素、（e）モリブデン酸塩、（f）トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、のうちのいずれかの、若しくは上記（e）及び/又は（f）に他の成分を複合添加した防錆添加成分（B）が配合され、必要に応じて、固形潤滑剤（C）及び硬化剤などが添加されるが、さらに必要に応じて、添加剤として、有機着色顔料（例えば、縮合多環系有機顔料、フタロシアニン系有機顔料など）、着色染料（例えば、有機溶剤可溶性アゾ系染料、水溶性アゾ系金属染料など）、無機顔料（例えば、酸化チタンなど）、キレート剤（例えば、チオールなど）、導電性顔料（例えば、亜鉛、アルミニウム、ニッケルなどの金属粉末、リン化鉄、アンチモンドープ型酸化錫など）、カップリング剤（例えば、シランカップリング剤、チタンカップリング剤など）、メラミン・シアヌル酸付加物などの1種又は2種以上を添加することができる。

【0091】また、上記被膜形成有機樹脂及び添加成分を含む被膜形成用の塗料組成物は、通常、溶媒（有機溶剤及び/又は水）を含有し、さらに必要に応じて中和剤などが添加される。有機被膜の乾燥膜厚は0.1～5μm、好ましくは0.3～3μm、さらに好ましくは0.5～2μmとする。有機被膜の膜厚が0.1μm未満では耐食性が不十分であり、一方、膜厚が5μmを超えると導電性、加工性が低下する。

【0092】次に、本発明の有機被膜鋼板の製造方法について説明する。本発明の有機被膜鋼板は、亜鉛めっき鋼板又はアルミニウム系めっき鋼板の表面を必要に応じて化成処理した後、上述した被膜形成有機樹脂（A）に対して、（a）Caイオン交換シリカ及びリン酸塩、（b）Caイオン交換シリカ、リン酸塩及び酸化ケイ素、（c）カルシウム化合物及び酸化ケイ素、（d）カルシウム化合物、リン酸塩及び酸化ケイ素、（e）モリブデン酸塩、（f）トリアゾール類、チオール類、チアジアゾール類、チアゾール類、チウラム類の中から選ばれる1種以上の有機化合物、のうちのいずれかの、若しくは上記（e）及び/又は（f）に他の成分を複合添加した防錆添加成分（B）が添加され、さらに必要に応じて固形潤滑剤（C）などが添加された塗料組成物を塗布し、加熱乾燥させることにより製造される。なお、めっき鋼板の表面は、上記化成処理液又は塗料組成物を塗布する前に必要に応じてアルカリ脱脂処理し、さらに密着性、耐食性を向上させるために表面調整処理などの前処理を施すことができる。

【0093】めっき鋼板表面に化成処理液をコーティングする方法としては、塗布方式、浸漬方式、スプレー方式のいずれでもよく、塗布方式ではロールコーター（3 50 ロール方式、2ロール方式など）、スクイズコーター、

各サンプルについて、日本パーカライジング（株）製のアルカリ処理液CLN-384S（80℃、スプレー2分）でアルカリ脱脂を行った後、上記の複合腐食試験（CCT）を行い、所定サイクル後の白錆面積率で評価した。評価基準は、以下の通りである。

◎：白錆発生なし

○+：白錆発生面積率5%未満

○：白錆発生面積率5%以上、10%未満

○-：白錆発生面積率10%以上、25%未満

△：白錆発生面積率25%以上、50%未満

×：白錆発生面積率50%以上

【0104】(4) 塗料密着性

各サンプルについて、メラミン系の焼付塗料（膜厚30μm）を塗装した後、沸水中に2時間浸漬し、直ちに基盤目（1mm間隔で10×10の基盤目）のカットを入れて、粘着テープによる貼着・剥離を行い、塗膜の剥離*

*面積率で評価した。評価基準は以下の通りである。

◎：剥離なし

○：剥離面積率5%未満

△：剥離面積率5%以上、20%未満

×：剥離面積率20%以上

【0105】(5) 加工性

ブランク径φ120mm、ダイス径φ50mmで深絞り成形（無塗油条件）を行い、割れが生ずるまでの成形高さを評価した。評価基準は以下の通りである。

◎：絞り抜け

○：成形高さ30mm以上

△：成形高さ20mm以上、30mm未満

×：成形高さ20mm未満

【0106】

【表1】

表1

No.	種 類	付着量 (g/m ²)
1	電気亜鉛めっき鋼板	20
2	溶融亜鉛めっき鋼板	60
3	合金化溶融亜鉛めっき鋼板 (Fe10wt%)	60
4	溶融 Zn-Al 合金めっき鋼板 (Al:55wt%)	90
5	溶融 Zn-5wt% Al-0.5wt% Mg 合金めっき鋼板	90
6	溶融アルミニウムめっき鋼板 (Al:6wt% Si 合金めっき)	60

【0107】

※ ※【表2】

表2

【化成処理条件】

No.	処理組成物			処理方法	膜厚	本発明条件の適否
	種類	商品名等	備考			
1	リチウムシリケート	日産化学工業製 LSS-35	SiO ₂ /LiO ₂ =5.5	塗布→150℃乾燥	0.5μm	満足する
2	リチウムシリケート	日産化学工業製 LSS-45	SiO ₂ /LiO ₂ =4.5	塗布→150℃乾燥	0.5μm	満足する
3	リチウムシリケート	日産化学工業製 LSS-75	SiO ₂ /LiO ₂ =7.5	塗布→150℃乾燥	0.5μm	満足する
4	リチウムシリケート	デュポン社製ポリシリケート40	SiO ₂ /LiO ₂ =4.6~5.0	塗布→150℃乾燥	0.5μm	満足する
5	リン酸塩処理	日本パーカライジング製 PB3312	—	スプレー→水洗・乾燥	2μm	満足する
6	有機樹脂皮膜	アクリル-エチレン共重合体	有機樹脂：エポキシ樹脂 =100:10	塗布→150℃乾燥	1μm	満足する
7	フィテン酸処理	三井化学製フィテン酸 10g/l 水溶液	—	塗布→150℃乾燥	0.5μm	満足する
8	タンニン酸処理	富士化学製タンニン AL10g/l 水溶液	—	塗布→150℃乾燥	0.5μm	満足する
9	高分子キレート化剤	ミヨシ化学工業製ジチオカルバミン酸アンモニウム塩	—	塗布→150℃乾燥	0.5μm	満足する
10	6価クロムフリー	亜硫酸クロム (III) + リン酸	リン酸/クロム=1.5	塗布→150℃乾燥	0.3μm	満足する
11	6価クロムフリー	亜硫酸クロム (III) + リン酸	リン酸/クロム=1.5	塗布→150℃乾燥	0.3μm	満足する
12	6価クロムフリー	亜硫酸クロム (III) + リン酸	リン酸/クロム=1.5	塗布→150℃乾燥	0.3μm	満足する
13	6価クロムフリー	亜硫酸クロム (III) + リン酸	リン酸/クロム=1.5	塗布→150℃乾燥	0.3μm	満足する

【0108】

【表3】

(重層部)
[0112]

* [表6]

*

表 6

No.	めっき 鋼板	第一層皮膜		第二層皮膜				乾燥 温度 (℃)	膜厚 (μm)	区 分
		皮 膜 組成物	樹脂 組成物	前添加成分 (B)		固形潤滑剤 (C)				
				種類	配合量	種類	配合量			
	#1	#2	#3	#4	#5	#5	#6			
1	1	1	1	15	15	—	—	140	1.5	本発明例
2	1	1	2	15	15	—	—	140	1.5	本発明例
3	1	1	3	15	15	—	—	140	1.5	本発明例
4	1	1	4	15	15	—	—	140	1.5	本発明例
5	1	1	5	15	15	—	—	140	1.5	本発明例
6	1	1	6	15	15	—	—	140	1.5	本発明例
7	1	1	7	15	15	—	—	140	1.5	本発明例
8	1	1	8	15	15	—	—	140	1.5	本発明例
9	1	—	1	15	15	—	—	140	1.5	本発明例
10	1	—	2	15	15	—	—	140	1.5	本発明例
11	1	—	3	15	15	—	—	140	1.5	本発明例
12	1	—	4	15	15	—	—	140	1.5	本発明例
13	1	—	5	15	15	—	—	140	1.5	本発明例
14	1	—	6	15	15	—	—	140	1.5	本発明例
15	1	—	7	15	15	—	—	140	1.5	本発明例
16	1	—	8	15	15	—	—	140	1.5	本発明例
17	1	1	1	—	—	—	—	140	1.5	比較例

[0113]

※ ※ [表7]

表 7

No.	外 観	性 能			区 分	
		耐白錆性 CCT 40サイクル後	アルカリ脱脂 後の耐白錆性 CCT 40サイクル後	塗 料 密着性		
1	○	◎	◎	◎	—	本発明例
2	○	◎	◎	◎	—	本発明例
3	○	○+	○	◎	—	本発明例
4	○	○+	○	◎	—	本発明例
5	○	○	○—	◎	—	本発明例
6	○	○	○—	◎	—	本発明例
7	○	○	○—	◎	—	本発明例
8	○	○	○—	◎	—	本発明例
9	○	◎	◎	◎	—	本発明例
10	○	◎	◎	◎	—	本発明例
11	○	○+	○	◎	—	本発明例
12	○	○+	○	◎	—	本発明例
13	○	○	○—	◎	—	本発明例
14	○	○	○—	○	—	本発明例
15	○	○	○—	○	—	本発明例
16	○	○	○—	○	—	本発明例
17	○	×	×	◎	—	比較例

[0114]

[表8]

表 10

No.	鋼 板	第一層皮膜		第二層皮膜						区 分
		皮 膜 組成物	樹 脂 組成物	防錆添加成分 (B)		固形溶剤系 (C)		乾燥 温度 (℃)	膜厚 (μm)	
				種類	配合量	種類	配合量			
	#1	#2	#3	#4	#5	#5	#6			
30	1	1	1	15	15	—	—	140	0.001	比較例
31	1	1	1	15	15	—	—	140	0.1	本発明例
32	1	1	1	15	15	—	—	140	0.5	本発明例
33	1	1	1	15	15	—	—	140	1.0	本発明例
34	1	1	1	15	15	—	—	140	2.0	本発明例
35	1	1	1	15	15	—	—	140	2.5	本発明例
36	1	1	1	15	15	—	—	140	3.0	本発明例
37	1	1	1	15	15	—	—	140	4.0	本発明例
38	1	1	1	15	15	—	—	140	5.0	本発明例
39	1	1	1	15	15	—	—	140	20.0	比較例

[0117]

* *【表11】

表 11

No.	外 観	性 能				区 分
		耐白錆性 CCT 40サイクル後	アルカリ樹脂 後の耐白錆性 CCT 40サイクル後	塗 料 密着性	溶 性	
30	○	×	×	◎	—	比較例
31	○	○—	○—	◎	—	本発明例
32	○	○—	○—	◎	—	本発明例
33	○	○	○	◎	—	本発明例
34	○	◎	◎	◎	—	本発明例
35	○	◎	◎	◎	—	本発明例
36	○	◎	◎	◎	—	本発明例
37	○	◎	◎	◎	—	本発明例
38	○	◎	◎	◎	—	本発明例
39	○	◎	◎	◎	—	比較例

※1

※1 溶接が不可能

[0118]

* *【表12】

表 12

No.	めっき 鋼板	第一層皮膜		第二層皮膜						乾燥 温度 (℃)	膜厚 (μm)	区 分
		皮 膜 組成物	樹 脂 組成物	防錆添加成分 (B)		固形溶剤系 (C)						
				種類	配合量	種類	配合量					
#1	#2	#3	#4	#5	#5	#6						
40	1	1	1	15	15	—	—	40	1.5	比較例		
41	1	1	1	15	15	—	—	50	1.5	本発明例		
42	1	1	1	15	15	—	—	80	1.5	本発明例		
43	1	1	1	15	15	—	—	120	1.5	本発明例		
44	1	1	1	15	15	—	—	150	1.5	本発明例		
45	1	1	1	15	15	—	—	200	1.5	本発明例		
46	1	1	1	15	15	—	—	230	1.5	本発明例		
47	1	1	1	15	15	—	—	250	1.5	本発明例		
48	1	1	1	15	15	—	—	350	1.5	本発明例		
49	1	1	1	15	15	—	—	380	1.5	比較例		

[0119]

50 【表13】

表 15

No.	外観	性 能				区 分
		耐白錆性	アルカリ脱脂後の耐白錆性	塗 料	加工	
		CCT	CCT	密着性	性	
		40 サイクル後	40 サイクル後			
50	○	○	○	◎	—	本発明例
51	○	○	○	◎	—	本発明例
52	○	○	○	◎	—	本発明例
53	○	○	○	◎	—	本発明例
54	○	○	○	◎	—	本発明例
55	○	○	○	◎	—	本発明例
56	○	○	○	◎	—	本発明例
57	○	○	○	◎	—	本発明例
58	○	○	○	◎	—	本発明例
59	○	○	○	◎	—	本発明例
60	○	○	○	◎	—	本発明例
61	○	○+	○+	◎	—	本発明例
62	○	○+	○+	◎	—	本発明例
63	○	○+	○+	×	—	本発明例

【0122】

* * 【表16】

表 16

No.	め き 鋼 板	第一層皮膜		第二層皮膜						区 分
		皮 膜 組成物	密 着 組成物	防錆油加成分 (B)		固形溶剤類 (C)		乾燥 温度 (℃)	膜厚 (μ m)	
				顔料	配合量	顔料	配合量			
	#1	#2	#3	#4	#5	#6	#7			
64	1	1	1	16	15	—	—	140	1.5	本発明例
65	1	1	1	17	15	—	—	140	1.5	本発明例
66	1	1	1	18	15	—	—	140	1.5	本発明例
67	1	1	1	19	15	—	—	140	1.5	本発明例
68	1	1	1	20	15	—	—	140	1.5	本発明例
69	1	1	1	21	15	—	—	140	1.5	本発明例
70a	1	1	1	1	15	1	10	140	1.0	本発明例
70b	1	1	1	5	15	1	10	140	1.0	本発明例
70c	1	1	1	7	15	1	10	140	1.0	本発明例
70d	1	1	1	12	15	1	10	140	1.0	本発明例
70e	1	1	1	13	15	1	10	140	1.0	本発明例
70f	1	1	1	14	15	1	10	140	1.0	本発明例
70g	1	1	1	15	15	1	10	140	1.0	本発明例
71	1	1	1	15	15	2	10	140	1.0	本発明例
72	1	1	1	15	15	3	10	140	1.0	本発明例
73	1	1	1	15	15	4	10	140	1.0	本発明例
74	1	1	1	15	15	5	10	140	1.0	本発明例
75	1	1	1	15	15	6	10	140	1.0	本発明例

【0123】

【表17】

表 19

No.	外 観	性 能				区 分
		耐白錆性	アルカリ脱脂	塗 料	加	
		CCT 40 サイクル後	後の耐白錆性 CCT 40 サイクル後	密着性	工 性	
76	○	◎	◎	◎	○	本発明例
77	○	◎	◎	◎	◎	本発明例
78	○	◎	◎	◎	◎	本発明例
79	○	◎	◎	○	◎	本発明例
80	○	◎	◎	×	◎	比較例
81	○	◎	◎	◎	—	本発明例
82	○	◎	◎	◎	—	本発明例
83	○	◎	◎	◎	—	本発明例
84	○	◎	◎	◎	—	本発明例
85	○	◎	◎	◎	—	本発明例
86	○	◎	◎	◎	—	本発明例
87	○	◎	◎	◎	—	本発明例
88	○	◎	◎	◎	—	本発明例

[0126]

20【表20】

表 20

No.	めっき鋼板	第一層皮膜		第二層皮膜						区 分	
		種 類	Cr 付着量 (金属 Cr 換算) #2 (mg/m ²)	樹 脂 組成物 #3	防錆添加成分 (B)		固形溶剤 (C)		乾燥 温度 #6 (°C)		膜厚 (μm)
					種類 #4	配合量 #5	種類 #5	配合量 #6			
89	1	10	50	1	15	15	—	—	140	0.8	本発明例
90	1	11	50	1	15	15	—	—	140	0.8	本発明例
91	1	12	50	1	15	15	—	—	140	0.8	本発明例
92	1	13	50	1	15	15	—	—	140	0.8	本発明例

[0127]

※ ※【表21】

表 21

No.	外 観	性 能				区 分
		耐白錆性	アルカリ脱脂	塗 料	加	
		CCT 50 サイクル後	後の耐白錆性 CCT 50 サイクル後	密着性	工 性	
89	○	◎	◎	◎	—	本発明例
90	○	◎	◎	◎	—	本発明例
91	○	○	○	◎	—	本発明例
92	○	○	○	◎	—	本発明例

[0128]

【発明の効果】以上述べたように本発明の有機被覆鋼板は、製造時の処理液や製品の皮膜成分中に6価クロムを

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F ターム (参考) 4D075 CA33 DB02 DB05 DB07 DC01
 DC12 DC18 EA17 EB33
 4F100 AA02E AA02H AA04E AA04H
 AA17 AA20E AA20H AB03A
 AB09E AB09H AB10A AB18A
 AB31 AH07E AH07H AJ11
 AJ11H AK01E AK04 AK04H
 AK16 AK18 AK18H AK36
 AK36H AK41 AK51 AK51H
 AK53 AK53E AK70 AK71
 AL06 AL06E AR00C BA02
 BA03 BA04 BA05 BA06 BA07
 BA10A BA10E BA13 CA02
 CA14 CA14E CA19 CA19E
 EH46 EH71 EH71A E142
 E168 E168C E186 GB07
 GB32 GB49 JAZ0E JB02
 JB13E JK06 JL01 JL02
 JM02E YY00E
 4J038 DB001 DB301 HA21E HA24E
 HA41E HA44E JB17 JB34
 JC02 JC1E NA03 PB05 PB07
 PC02
 4K026 AA02 AA07 AA09 AA12 AA13
 AA22 BA01 BA02 BA03 BA08
 BB04 BB06 BB08 BB09 CA02
 CA16 CA23 CA29 CA36 CA37
 CA39 CA41 DA15 DA16
 4K044 AA02 AB02 BA10 BA14 BA17
 BA21 BB03 BB04 BC02 BC04
 BC05 CA11 CA18 CA53
 4K062 AA01 BA08 BA10 BA14 BB18
 BB21 BB22 BC07 BC09 BC12
 BC15 BC19 CA02 CA04 FA12
 FA16 GA08

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-335955

(43)Date of publication of application : 07.12.2001

(51)Int.Cl. C23C 22/07
B05D 3/10
B05D 7/14
B05D 7/24
B32B 15/08
B32B 15/18
B32B 27/38
C09D 5/08
C09D163/00
C09D201/00
C23C 22/40
C23C 22/42
C23C 26/00
C23C 28/00
C23F 11/00

(21)Application number : 2000-161050

(71)Applicant : NKK CORP

(22)Date of filing : 30.05.2000

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(54) ORGANIC COMPOUND COATED STEEL SHEET EXCELLENT IN CORROSION
RESISTANCE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an organic compound coated steel sheet safe and harmless to a person in the production and also utilization, and excellent in corrosion resistance.

SOLUTION: The surface of a galvanized steel sheet or an aluminum-based plated steel sheet is provided with an organic film containing any rust preventive addition component (B) selected from (a) Ca ion-exchanged silica and phosphate, (b) Ca ion-exchanged silica, phosphate and silicon oxide, (c) a calcium compound and silicon oxide, (d) a calcium compound, phosphate and silicon oxide, (e) molybdate, (f) one or more kinds of organic compounds selected from triazoles, thiols, tiadiazoles, tiazoles and thiurams by 1 to 100 pts.wt. in total (solid content) to 100 pts.wt. (solid content) of a film forming organic resin (A).

LEGAL STATUS

[Date of request for examination] 04.03.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]	3911965
[Date of registration]	09.02.2007
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

In the drawings, any words are not translated.

claim 6] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, carry out 1-100 weight section (solid content) content of following (a) and the rust-proofing addition component (B) of (f) in total to the coat formation organic (resin A) 100 weight section (solid content). (a) Organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat one or more sorts of whose organic compound

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[Claim 13] The organic covering steel plate excellent in the corrosion resistance according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 characterized by having the chemical conversion coat which does not contain hexavalent chromium on the front face of a zinc system plating steel plate or an aluminum system plating steel plate, and having an organic coat on it at the upper layer.

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DETAILED DESCRIPTION

Detailed Description of the Invention

[0001]

Field of the Invention] since it be adapted for environmental problems, such as volatilization, etc., of the effect on the operator and user who deal with a product about the optimal zinc covering steel plate for an automobile, a household electric appliances, a building materials application, etc., the cure against waste water treatment at the time of manufacture, and the harmful matter from the product under an operating environment further, this invention relate to the environmental ead surface treated steel sheet which do not contain heavy metal, such as chromium harmful to an environment and the body, lead, cadmium, and mercury, at all the time of manufacture, and a product.

[0002]

description of the Prior Art] From the former, the steel plate with which chromate treatment in the processing liquid which used a chromic acid, dichromic acid, or its salts as the major component was performed is broadly used for the front face of a zinc system plating steel plate an aluminum system plating steel plate at the steel plate for home electronics, the steel plate building materials, and the steel plate for automobiles in order to raise corrosion resistance (i.e., rust-proof, rust-proof nature). This chromate treatment is the economical art which can performed comparatively easily [exel in corrosion resistance and].

[0003] Although chromate treatment uses the hexavalent chromium which is the public nuisance material from this hexavalent chromium being processed with a closed system in down stream processing, and it being returned and collected completely, and not being emitted to a nature, chromium elution out of a chromate film being mostly made to zero according to a nature, generation by the organic coat. However, the motion which is going to reduce use of heavy metal including hexavalent chromium independently from the latest global environment problems is pressing. Moreover, when the shredder dust of an abandonment product is abandoned, in order product, the motion which is going to reduce this has also started.

[0004] Since it is such, in order to prevent generating of the white rust of a zinc system plating steel plate, many pollution-free processing techniques by chromate treatment and so-called chromium free techniques are proposed. Among these, some approaches using an organic stem compound or organic resin are also proposed, for example, the following approaches can mentioned.

[0005] (1) The approach using a tannic acid (for example, JP 51-71233A)

) The approach using the thermosetting coating which mixed the tannic acid with an epoxy sin and amino resin (for example, JP 63-90581A)

) How [0006] to use the chelate force of tannic acids, such as an approach (for example, JP 9-5760A) using the mixed constituent of drainage system resin and multiple-valued phenolic acid (4) The surface treatment approach which applies a hydrazine derivative water solution to e front face of a tin plate or a galvanized steel plate (for example, JP 53-27594B, JP 56-1286B)

(5) The approach using the rust-preofer containing the amine addition salt which was made to add an amine to the mixture of acyl ZARUKOSHIN and a benzothiazole SOL, and was obtained (for example, JP 53-130284A)

(6) The approach using the processing agent which mixed a heterocyclic compound and tannic acids, such as a benzothiazole compound, (for example, JP 57-198267A) [0007]

[Problem(s) to be Solved by the Invention] However, there is a trouble which is described below in these conventional techniques. First, each approach of above-mentioned (1) - (4) has a problem in respect of corrosion resistance. This has a cause in the coat obtained having the self-repair effectiveness by neither of the approaches. That is, with a chromate film, it is (a). The barrier effectiveness: The obstruction effectiveness over corrosion factors (water, oxygen, chlorine, etc.) with a trivalent Cr subject's poorly soluble compound (hydration oxide) (b) The self-repair effectiveness: Discover advanced corrosion resistance according to the synergistic effect of both of the protective film formation effectiveness in the corrosion origin by 6 ** Cr. However, with the conventional chromium free technique, even if not depended on chromium about the barrier effectiveness, organic resin etc. could give to some extent, but about the self-repair effectiveness, since the self-repair nature manifestation matter used as an alternative of 6 ** Cr was not offered, advanced corrosion resistance was unrealizable.

[0008] Moreover, the corrosion resistance of the approach of the above (1) is not only inadequate, but the uniform appearance after processing is not acquired. Moreover, it is not a thing with an eye on especially the approach of the above (2) forming a thin film-like (0.1-5 micrometers) rust-proofing coat in a zinc system or an aluminum system plating front face directly, and even if it applies to a zinc system or an aluminum system plating front face in the shape of a thin film for this reason, sufficient corrosion prevention effectiveness is not acquired. Moreover, corrosion resistance is inadequate similarly about the approach of the above (3). [0009] The approach of the above (4) is not what was applied about the zinc system or the aluminum system plating steel plate, and even if it applies to a zinc system or an aluminum system plating steel plate, since the coat obtained does not have the network structure, it will not have sufficient barrier nature, and its corrosion resistance will be still more inadequate for this reason. Moreover, although mixing water soluble polymer compounds (poly-vinyl alcohol, a maleate copolymer, acrylic ester copolymer, etc.) in a hydrazine derivative water solution with an eye on the homogeneous improvement in a coat is indicated by JP 53-23772B and JP 56-10355B, corrosion resistance sufficient with the mere mixture of a hydrazine derivative water solution and a water soluble polymer compound is not acquired.

[0010] Furthermore, the corrosion resistance which was not a thing with an eye on the approach of the above (5) and (6) also forming a rust-proofing coat in a zinc system or an aluminum system plating steel plate front face for a short time, and was excellent since there was no barrier nature to corrosion factors, such as oxygen and water, even if it applied the processing agent to the plating steel plate front face is not acquired. Moreover, although mixing with resin (an epoxy resin, acrylic resin, urethane resin, nitrocellulose resin, vinyl chloride resin, etc.) is also described as an additive about the approach of (6), corrosion resistance sufficient with the mere mixture of heterocyclic compounds, such as a benzothiazole compound, and resin is not acquired.

[0011] Moreover, in order to remove the oil applied to the front face by press working of sheet metal etc., each approach of above-mentioned (1) - (6) is set on practical use conditions which perform with a pH [by a spray etc.] of about nine to 11 alkaline degreasing, and a coat is exfoliated or damaged with alkaline degreasing, and it has the problem that corrosion resistance cannot be held. Therefore, these approaches are not what was suitable for practical use as an approach of forming a rust-proofing coat. Therefore, the purpose of this invention solves the technical problem of such a conventional technique, and is to offer the organic covering steel plate with which insurance and the corrosion resistance which was harmless and was moreover excellent are acquired excluding heavy metal, such as hexavalent chromium, in a coat also in case it is used, a production process and.

[0012]

means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of this invention persons' inquiring wholeheartedly, after forming in the front face of a zinc system plating steel plate or an aluminum system plating steel plate the chemical conversion coat which does not contain hexavalent chromium if needed by forming the organic coat which tried out optimum dose combination of the specific self-repair nature manifestation matter (rust-proofing addition component) which replaces hexavalent chromium into coat formation organic resin. Without performing chromate treatment with a possibility of having a bad influence on environment or the body, it was pollution-free and found out that the organic covering steel plate which was extremely excellent in corrosion resistance was obtained. The configuration by which this invention was made based on such knowledge, and it is characterized he] is as follows.

[13] [1] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, carry out 1-100 weight section (solid content) content of the rust-proofing addition component (B) of either of following (a) - (f) in total to the coat formation organic (resin A) 100 weight section (solid content), (a) calcium ion-exchange silica and a phosphate (b) calcium ion-exchange silica, phosphate, a silicon oxide (c) lime compound, and a silicon oxide (d) lime compound. The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat one or more sorts of whose organic compound thickness chosen from phosphate and silicon oxide (e) molybdate (f) triazoles, thiols, thiazoles, and thiurams 0.1-5 micrometers.

[14] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, the coat formation organic (resin A) 100 weight section (solid content) is received. [2] Following (e), (g) And carry out 1-100 weight section (solid content) content of the rust-proofing addition component (B) of (h) in total. (e) Organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat molybdate (g) calcium, lime compound (h) phosphate, and/or whose silicon oxide thickness are 0.1-5 micrometers.

[15] [5] The organic covering steel plate excellent in the corrosion resistance characterized to have the organic coat which carries out 1-100 weight section (solid content) content of following (e) and the rust-proofing addition component (B) of (i) in total to the coat formation organic (resin A) 100 weight section (solid content), and whose (e) molybdate (i) calcium ion-exchange silica thickness is 0.1-5 micrometers on the front face of a zinc system plating steel plate or an aluminum system plating steel plate.

[16] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, the coat formation organic (resin A) 100 weight section (solid content) is received. [4] Following (f), (g) And carry out 1-100 weight section (solid content) content of the rust-proofing addition component (B) of (h) in total. (f) Triazoles, thiols, thiazoles, and thiurams. The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat one or more sorts of whose organic compound (g) calcium, lime compound (h) phosphate, d/or silicon oxide thickness which are chosen from thiurams are 0.1-5 micrometers.

[17] [5] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, carry out 1-100 weight section (solid content) content of following (f) and the rust-proofing addition component (B) of (i) in total to the coat formation organic (resin A) 100 weight section (solid content). (f) Organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat one or more sorts of whose (organic compound i) calcium ion-exchange silica thickness chosen from triazoles, thiols, thiazoles, and thiurams is 0.1-5 micrometers.

[18] [6] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, carry out 1-100 weight section (solid content) content of following (e) and the rust-proofing addition component (B) of (f) in total to the coat formation organic (resin A) 100 weight section (solid content). (e) Organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat one or more sorts of whose organic compound thickness chosen from molybdate (f) triazoles, thiols, thiazoles, and thiurams is 0.1-5 micrometers.

[19] On the front face of a zinc system plating steel plate or an aluminum system plating steel

plate, the coat formation organic (resin A) 100 weight section (solid content) is received. [7] Following (e), Carry out 1-100 weight section (solid content) content of the rust-proofing addition component (B) of (f), (g), and (h) in total. (e) Molybdate (f) triazoles, thiols, and thiazoles. The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat one or more sorts of whose organic compound (g) calcium, lime compound (h) phosphate, and/or silicon oxide thickness which are chosen from thiurams and thiurams are 0.1-5 micrometers.

[20] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, the coat formation organic (resin A) 100 weight section (solid content) is received. [8] Following (e), (f) And carry out 1-100 weight section (solid content) content of the rust-proofing addition component (B) of (i) in total. (e) Organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat one or more sorts of whose (organic compound i) calcium ion-exchange silica thickness chosen from molybdate (f) triazoles, thiols, thiazoles, and thiurams is 0.1-5 micrometers.

[202] [9] The above [1] Organic covering steel plate the organic coat excellent [steel plate] in the corrosion resistance characterized by the content of this solid lubricant (C) being 1 - 80 weight section (solid content) to the coat formation organic (resin A) 100 weight section (solid content) including solid lubricant (C) further in one organic covering steel plate of - [8].

[10] The above [1] Organic covering steel plate excellent in the corrosion resistance characterized by coat formation organic resin (A) being organic macromolecule resin which has an OH radical and/or a COOH radical in one organic covering steel plate of - [9].

[2022] [11] The organic covering steel plate which was excellent in the corrosion resistance characterized by organic macromolecule resin being thermosetting resin in the organic covering steel plate of the above [10].

[12] The organic covering steel plate which was excellent in the corrosion resistance characterized by thermosetting resin being an epoxy resin and/or a modified epoxy resin in the organic covering steel plate of the above [11].

[13] The above [1] Organic covering steel plate excellent in the corrosion resistance characterized by having the chemical conversion coat which does not contain hexavalent chromium on the front face of a zinc system plating steel plate or an aluminum system plating steel plate in one organic covering steel plate of - [12], and having an organic coat in the upper layer.

[2023] After forming in the front face of a zinc system plating steel plate or an aluminum system plating steel plate the chemical conversion coat which does not contain hexavalent chromium if needed, the fundamental description of the organic covering steel plate of this invention coat formation organic resin (A) and the organic macromolecule resin (further --- desirable --- thermosetting resin ---) which has an OH radical and/or a COOH radical preferably to an epoxy resin and/or a modified epoxy resin, preferably especially as self-repair nature manifestation matter (rust-proofing addition component) (a) calcium ion-exchange silica and phosphate, (b) calcium ion-exchange silica, phosphate and silicon oxide, (c) lime compound, and silicon oxide, (d) A lime compound, phosphate and silicon oxide, (e) molybdate, (f) Triazoles, thiols, thiazoles, and thiurams one or more sorts of organic compounds chosen from thiurams, and ** --- it is in the point in which the organic coat which blended with inner either or the above (e), and/or (f) the rust-proofing addition component (B) which carried out compound addition of other components was formed.

[2024] In this invention, in an organic coat, as mentioned above (a) calcium ion-exchange silica and a phosphate (b) calcium ion-exchange silica, phosphate, a silicon oxide (c) lime compound, and a silicon oxide (d) lime compound, phosphate and silicon oxide (e) molybdate (f) triazoles. Either of one or more sorts of organic compounds chosen from thiols, thiazoles, and thiurams, Or the anti-corrosiveness (the self-repair effectiveness) which was especially excellent in the above (e) and/or (f) by carrying out optimum dose combination of the rust-proofing addition component (B) which carried out compound addition of other components, and the (self-repair nature manifestation matter) can be obtained. The corrosion prevention device acquired by having blended the component of above-mentioned (a) - (f) into such an organic

at is considered as follows.

[025] First, the component of above-mentioned (a) ~ (d) discovers self-repair nature according to a precipitate operation, and is considered that the reaction mechanism progresses at the following steps.

1st step: **** calcium carries out the priority dissolution under corrosive environment other than zinc and aluminum which are a plating metal.

2nd step: In the case of phosphate, the calcium ion to which the calcium ion which carried out the priority dissolution at the phosphoric-acid ion dissociated by the hydrolysis reaction and the 1st step of the above carried out the priority dissolution of the complexation reaction at the 1st step of the above on the front face in the case of a lifting and silicon oxide adsorbs, and try out electric neutralization of the surface charge, and condense it. Consequently, in any case, a precise and poorly soluble protective film generates, and corrosion reaction is controlled when this blocks a corrosion origin.

[026] Moreover, the component of the above (e) discovers self-repair nature according to the dissolution effectiveness. That is, a precise oxide is formed in a plating coat front face with dissolved oxygen under corrosive environment, and corrosion reaction is controlled when this blocks a corrosion origin. Moreover, the component of the above (f) discovers self-repair nature according to an adsorption effect. That is, it sticks to the polar group in which the zinc eluted by corrosion and aluminum contain the nitrogen which the component of the above (f) has, and thus, an inactive coat is formed, and corrosion reaction is controlled when this blocks a corrosion origin.

[027] moreover, the organic macromolecule resin (desirable -- thermosetting resin --) which has an OH radical and/or a COOH radical to the coat formation organic resin (A) of an organic resin in which the corrosion prevention operation by the above self-repair nature manifestation matter. By using an epoxy resin and/or a modified epoxy resin still more preferably use this organic giant-molecule resin forms precise barrier layer anodic oxide coating by the action with a cross linking agent, and this barrier layer anodic oxide coating is excellent in the transparency control ability of corrosion factors, such as oxygen, and firm bonding strength with base is acquired by the OH radical and COOH radical in a molecule, the especially excellent corrosion resistance (barrier nature) is acquired.

[028] moreover, considering the self-repair effectiveness acquired by each component of above-mentioned (a) ~ (d), (e), and (f). For obtaining more advanced self-repair nature, the above (a) and/or (f) are used as an indispensable component. It is desirable to adjust the rust-proofing addition component (V) of the following combination which compounded other components with is (combination), and the self-repair nature (namely, white-rust-proof) especially, most advanced when it is following (6) and (7) is obtained.

[029] (1) (e) molybdate, (g) calcium, and/or a lime compound. And rust-proofing addition component which blended (h) phosphate and/or silicon oxide (2) (e) molybdate. And rust-proofing addition component which blended (i) calcium ion-exchange silica (3) (f) triazoles. One or more sorts of organic compounds chosen from thiols, thiadiazole, thiazoles, and thioamides, (g) calcium and/or a lime compound and (h) phosphate, and/or silicon oxide. Blended rust-proofing addition component (4) One or more sorts of organic compounds chosen from (f) triazoles, thiols, thiadiazole, thiazoles, and thioamides, and rust-proofing addition component which blended (i) calcium ion-exchange silica [0030] (5) (e) molybdate and (f) triazoles, thiols. One or more sorts of organic compounds chosen from thiadiazole, thiazoles, and thioamides. Blended rust-proofing addition component (6) (e) molybdate and (f) triazoles. One or more sorts of organic compounds chosen from thiols, thiadiazole, thiazoles, and thioamides, (g) calcium and/or a lime compound and (h) phosphate, and/or silicon oxide. Blended rust-proofing addition component (7) One or more sorts of organic compounds chosen from (e) molybdate, (f) triazoles, thiols, thiadiazole, thiazoles, and thioamides, and rust-proofing addition component which blended (i) calcium ion-exchange silica [0031]

indifferent of the invention. Hereafter, the detail and its reason for limitation of this invention is explained. As a zinc system plating steel plate used as the base of the organic covering steel plate of this invention A galvanized steel sheet, a Zn-nickel alloy-plating steel plate, a Zn-Fe

alloy-plating steel plate (an electroplating steel plate and alloying hot-dip zinc-coated carbon steel sheet), A Zn-Cr alloy-plating steel plate, a Zn-Mn alloy-plating steel plate, a Zn-Co alloy-plating steel plate, A Zn-Co-Cr alloy-plating steel plate, a Zn-Cr-nickel alloy-plating steel plate, A Zn-Cr-Fe alloy-plating steel plate, a Zn-aluminum alloy-plating steel plate. For example, (a Zn-Silicon alloy-plating steel plate, a Zn-Silicon-Mg alloy-plating steel plate), A Zn-Mg alloy-plating steel plate, a Zn-aluminum-Mg plating steel plate, the zinc system composite-coatings steel plate (for example, Zn-SiO₂ distribution plating steel plate) that distributed the metallic oxide, the polymer, etc. in the plating coat of these plating steel plates can be used further. [0032] Moreover, the double layer plating steel plate which galvanized congener or a thing of a different kind more than two-layer among the above plating can also be used. Moreover, as an aluminum system plating steel plate used as the base of the organic covering steel plate of this invention, an aluminum plating steel plate, an aluminum-Si alloy-plating steel plate, etc. can be used. Moreover, as a plating steel plate, plating with half-closed eyes, such as nickel, may be beforehand performed to a steel plate side, and the various above plating may be performed on it. As the plating approach, which approach among an electrolytic decomposition process (electrolysis in a water solution or electrolysis in a non-aqueous solvent), scorification, and gaseous-phase methods which can be enforced is also employable.

[0033] Moreover, since it is made for neither a coat defect nor nonuniformity to arise when a bilayer coat which is mentioned later is formed in a plating coat front face, alkaline degreasing, solvent degreasing, surface control processing (alkaline surface control processing, acid surface control processing), etc. can be beforehand processed on a plating coat front face if needed. Moreover, surface control processing by the acidity or the alkaline water solution which contains an iron-group metal ion (nickel ion, Co ion, Fe ion) on a plating coat front face beforehand if needed can also be performed in order to prevent the black discoloration (a kind of the oxidation phenomenon on the front face of plating) under the operating environment of an organic covering steel plate. Moreover, when using an electrolytic zinc-coated carbon steel sheet as a substrate steel plate, an iron-group metal ion (nickel ion, Co ion, Fe ion) can be added to an electroplating bath in order to prevent black discoloration, and 1 ppm or more of these metals can be made to contain in a plating coat. In this case, there is especially no limit about the upper limit of the iron-group metal concentration in a plating coat.

[0034] Chemical conversion coats other than a chromate film (chemical conversion coat containing hexavalent chromium), i.e., the chemical conversion coat which does not contain hexavalent chromium, can be formed in the front face of a zinc system plating steel plate or an aluminum system plating steel plate if needed. This chemical conversion coat controls the activity of a plating steel plate, it is not formed in order to improve corrosion resistance and adhesion, and if it is the chemical conversion coat which does not contain hexavalent chromium, there will be no limit in that class.

[0035] Inorganic system coats, such as a mill scale which consists of multiple oxide coat (5) titanium oxide which consists of alkali silicate processing coat (4) chromium which consists of an alkali-metal oxide and silicon oxide, such as passivation films, such as a (1) phosphate processing coat (2) MORIBU date or a tongue state processing coat, and a phosphoric acid / molybdo-acid processing coat, and (3) lithium oxide, as a chemical conversion coat which does not contain hexavalent chromium, for example, and a zirconium dioxide, are applicable.

[0036] In addition, as a multiple oxide coat which consists of chromium of the above (4), the multiple oxide coat which consists of the oxide of chromium: a hydroxide, and oxide, such as a silica, an alumina, a titania, a zirconia, and a zinc oxide, is equivalent to it. Moreover, although not limited especially about the manufacture approach, it is effective to use water-soluble chromic compounds as processing liquid. Although there will be especially no limitation, for example, a chromium chloride, a chromium sulfate, chromium acetate, formic-acid chromium, etc., will be mentioned as these water-soluble chromic compounds if it is a water-soluble thing, carboxylic-acid chromium, such as chromium acetate and formic-acid chromium, is especially desirable. Moreover, as oxides, such as a silica, an alumina, a titania, a zirconia, and a zinc oxide, it is desirable to add the colloid and/or the powder of these oxides in processing liquid.

[0037] Moreover, the compound coat which blended organic resin into one inorganic system coat

for example, the chelate formation organic coat (8) above (1) of (6) thin-film organic resin at (0.1-2 micrometers of thickness) or an organic compound silicate coat (7) tannic acid, citric acid, phosphoric acid, etc., (2), and (3) in addition to the above-mentioned inorganic stem coat is applicable. The refractory sex skin film (for example, alkali silicate coat etc.) which contains silicon oxide also especially in the above is the most desirable from a viewpoint which controls zincy white rust.

[0038] Into the above-mentioned chemical conversion coat, organic resin can be further blended for the purpose of raising the workability of a coat, and corrosion resistance. As this organic resin, one sort, such as an epoxy resin, urethane resin, acrylic resin, an acrylic-ethylene copolymer, an acrylic-styrene copolymer, alkyl resin, polyester resin, and ethylene resin, or two or more can be used. These can be introduced into a coat as water-soluble resin and/or water-dispersible resin. Furthermore, it is effective to use together a water-soluble epoxy resin, water-soluble phenol resin, water-soluble butadiene rubber (SBR, NBR, MBR), melamine resin, polyisocyanate, an oxazoline compound, etc. as a cross linking agent in addition to these single system resin.

[0039] In the above-mentioned chemical conversion coat, as an additive for raising corrosion resistance further furthermore, a polyphosphate and phosphate (for example, phosphoric acid and phosphoric acid 2 hydrogen aluminum ---) molybdate, such as phosphorous acid zinc, polydiphosphate A (polydiphosphoric acid aluminum etc. and organic phosphorus) acid and salt [for example,] for example, phytic acid, a phytic acid salt, phosphoric acid, phosphonate, and these metal salts --- An alkali-metal salt etc. may blend one sort, such as organic inhibitor for example, a hydrate derivative, thiol compounds, dithiocarbamate, etc.) and organic compounds (for example, polyethylene glycol etc.), or two sorts or more.

[0040] furthermore --- as other additives --- an organic color pigment (for example, a condensed dye-dye system organic pigment ---) coloring colors (for example, organic solvent fusibility azo dye ---), such as a phthalocyanine system organic pigment inorganic pigments, such as a water-soluble azo metal color (for example, titanium oxide etc.), chelating agents (for example, thiol etc.) and a conductive pigment (for example, zinc ---) Metal powder, such as aluminum and nickel, iron-zinc iron, antimony doping metal tin oxide, etc. can also add one sort, such as coupling agents (for example, a silane coupling agent, a titanium coupling agent, etc.) and a melamine auric acid addition product, or two sorts or more.

[0041] Moreover, in the above-mentioned chemical conversion coat, one or more sorts of an iron-group metal ion (nickel ion, Co ion, Fe ion) may be added in order to prevent the black coloration (a kind of the oxidation phenomenon on the front face of plating) under the operating environment of an organic covering steel plate. Addition of nickel ion is the most suitable especially. In this case, as concentration of an iron-group metal ion, if there are or are [100000] 1/M in a processing constituent, desired effectiveness will be acquired.

though especially the upper limit of iron-group ion concentration is not defined, it is desirable consider as extent which does not affect corrosion resistance with the increment in concentration. The thickness of these chemical conversion coats may be 3 micrometers or less, even thickness exceeds 3 micrometers, it is for workability and conductivity to fail. Although specially a minimum does not set, it should just be taken as the thickness in which the corrosion-resistant improvement effectiveness is accepted.

[0042] After forming the above-mentioned chemical conversion coat if needed, the organic coat retaining the specific self-repair nature manifestation matter is formed in the front face of a system plating steel plate or an aluminum system plating steel plate. Although there is specially no limit as base resin of an organic coat and both water-soluble resin water-dispersible resin and organic solvent fusibility resin can be used, from a corrosion resistance viewpoint, it is specially desirable to use the organic macromolecule resin (A) which has an OH radical and/or COOH radical. Moreover, also in it, thermosetting resin is desirable and an epoxy resin or a modified epoxy resin is still more desirable.

[0043] As organic macromolecule resin which has an OH radical and/or a COOH radical, two or more sorts of mixture or addition polymerization objects of an epoxy resin, polyhydroxy polyether resin, the acrylic copolymer resin, the ethylene-acrylic-acid copolymer resin, an alkyl resin, a

polybutadiene resin, phenol resin, polyurethane resin, polyamine resin, polyphenylene resin, and these resin etc. are mentioned, for example.

[0044] (1) the epoxy resin which added propylene oxide, ethyleneoxide, or a polyalkylene glycol to the epoxy resin and bisphenol A which glycidyl-ether-ized bisphenol A, Bisphenol F, the novolak, etc. as an epoxy resin epoxy resin, and was glycidyl-ether-ized --- an aliphatic series epoxy resin, an alicyclic group epoxy resin, a polyether system epoxy resin, etc. can be used further. Especially these epoxy resins have a with a number average molecular weight of 1500 or more desirable thing, when it needs hardening at low temperature. In addition, the above-mentioned epoxy resin can also mix and use independent or a different thing of a class.

[0045] As a modified epoxy resin, the resin which made various modifiers react to the epoxy group or BDOHOKISHIPU radical in the above-mentioned epoxy resin is mentioned. For example, the amine addition urethane modified epoxy resin which added isocyanate to the epoxy acrylate resin which denaturalized with the epoxy ester resin to which the carboxyl group in a drying-oil fatty acid was made to react, the acrylic acid, the methacrylic acid, etc., the urethane modified epoxy resin to which the isocyanate compound was made to react, and the urethane modified epoxy resin which made the isocyanate compound react to an epoxy resin can be mentioned.

[0046] The above-mentioned polyhydroxy polyether resin is a polymer which is made to carry out the polycondensation of the dihydric phenol of a single karyotype or two karyotypes, or the mixed dihydric phenol of a single karyotype and two karyotypes to the epichlorhydrin of an equimolecular amount mostly under existence of an alkali catalyst, and is obtained. Resorcinol, hydroquinone, and a catechol are mentioned as an example of representation of single karyotype dihydric phenol, bisphenol A is mentioned as an example of representation of 2 karyotype phenol, and these may be used independently or may use two or more sorts together.

[0047] (2) As urethane resin urethane resin, oil denaturation polyurethane resin, alkyl system polyurethane resin, polyester system polyurethane resin, polyether system urethane resin, polycarbonate system polyurethane resin, etc. can be mentioned, for example.

(3) alkyl resin alkyl resin --- carrying out --- for example, oil modified alkyl resin, resin modified alkyl resin, phenol modified alkyl resin, styrene alkyl resin, silicon modified alkyl resin, acrylic modified alkyl resin, oil free alkyl resin, the amount of oil of macromolecules free alkyl resin, etc. can be mentioned.

[0048] (4) As acrylic resin acrylic resin, polyacrylic acid and its copolymer, polyacrylic ester and its copolymer, polymethacrylic acid ester and its copolymer, polymethacrylic acid ester and its copolymer, an urethane-acrylic-acid copolymer (or urethane denaturation acrylic resin), a styrene-acrylic-acid copolymer, etc. are mentioned, and the resin which denatured these resin with other alkyl resin, an epoxy resin, phenol resin, etc. further may be used, for example.

[0049] (5) Ethylene resin (polyolefin resin)

As ethylene resin, ethylene system copolymers, such as an ethylene-acrylic-acid copolymer, an ethylene-methacrylic-acid copolymer, and carboxyl denaturation polyolefin resin, an ethylene-unsaturated-carboxylic-acid copolymer, an ethylene system ionomer, etc. are mentioned, and the resin which denatured these resin with other alkyl resin, an epoxy resin, phenol resin, etc. may be used further, for example.

(6) As acrylic silicon resin acrylic silicon resin, what added the curing agent at this is mentioned to the side chain or end of an acrylic copolymer including a hydrolysis nature siloxy silyl radical as base resin, for example. The outstanding weatherability can be expected when these acrylic silicon resin is used.

[0050] (7) As a fluororesin fluororesin, there is a fluoro olefin system copolymer and there is a copolymer to which copolymerization of alkyl vinyl ether, synchro alkyl vinyl ether, carboxylic-acid denaturation vinyl ester, the hydroxyalkyl alkyl compound ether, tetrafluoro propyl vinyl ether, etc. and the fluorine monomer (fluoro olefin) was carried out as a monomer in this. When these fluororesins are used, the outstanding weatherability and the outstanding hydrophobicity can be expected.

[0051] Moreover, the core shell mold water-dispersion resin which consists of resin of a resin class which is different in the core part and shell part of a resin particle with an eye on low-

temperature-izing of the drying temperature of resin, or a different glass transition temperature is used. Moreover, the bridge formation between particles which used generation of the anion group by hydrolysis of alkoxysilane and the dehydration condensation reaction of the isoxallene radical to a resin particles, using the water-dispersion resin which has self-cross-linking. Moreover, the organic compound silicate which made organic resin compound-ize with a silica through a silane coupling agent as resin used for an organic coat is also suitable.

[0052] It is desirable to use especially thermosetting resin in this invention with an eye on improvement in the corrosion resistance of an organic coat or workability. In this case, curing agents, such as amino resin, such as urea-resins (butyl-ized urea-resin etc.), melamine resin (stylated melamine resin), a butyl-ized urea and melamine resin, and benzoguanamine resin, alk isocyanate, an oxazoline compound, and phenol resin, can be blended.

[0053] In the organic resin described above, if corrosion resistance, workability, and paintwork taken into consideration, an epoxy resin and ethylene resin are desirable and especially the thermosetting epoxy resin and thermosetting modified epoxy resin that have the cutoff nature which was excellent to corrosion factors, such as an enzyme, especially are suitable. As these thermosetting resin, an addition product or a condensate of a thermosetting epoxy resin, a thermosetting modified epoxy resin, an epoxy group content monomer and the copolymerized vinyl copolymer resin, the polybutadiene resin that has an epoxy group, the polyurethane resin which has an epoxy group, and these resin etc. can be mentioned, it is independent, or two or more sorts can be mixed and one sort of these epoxy group content resin can be used.

[0054] The rust-proofing addition component of either of following (a) - (f) which is the self-silica nature manifestation matter in an organic coat in this invention (B), (a) calcium ion-exchange silica and a phosphate (b) calcium ion-exchange silica, phosphate, a silicon oxide (c) is compound, and a silicon oxide (d) line compound. The rust-proofing addition component (B) which blended other components with one or more sorts of organic compounds chosen from phosphate and silicon oxide (e) molybdate (f) triazoles, thiols, thiazoles, thiazoles, and thiazams the above (a) and/or (f) is added. These components (a) it is as having described the corrosion prevention device by - (f) previously.

[0055] The above-mentioned component (a) and calcium ion-exchange silica contained in (b) are at fixed calcium ion in the front face of porous silica gel powder, and calcium ion is emitted under corrosive environment and it forms precipitation membrane. Although the thing of citration can be used as a calcium ion-exchange silica, the thing 4 micrometers or less of an particle diameter is desirably desirable, for example, it can use 6 micrometers or less of an particle diameter is 2-4 micrometers. If the mean particle diameter of calcium ion-exchange silica exceeds 6 micrometers, while corrosion resistance will fall, the distributed stability in the inside of a coating constituent falls.

[0056] As for calcium concentration in calcium ion-exchange silica, it is desirable more than 4% and that it is 2 - 3wt% desirably. Less than 1 wt%], the rust-proofing effectiveness according [calcium concentration] to calcium emission is not fully acquired. In addition, it is not fitted about the surface area of calcium ion-exchange silica, pH, and especially oil absorption. [0057] As above calcium ion-exchange silica it is SHILED EX C303 (the mean particle diameter 2.5-3.5 micrometers) made from W.R.Grace&Co. at a trade name, calcium concentration 3wt%, SHILED EX A03 (the mean particle diameter of 2.3-3.1 micrometers) calcium concentration 6wt%, SHILED EX AC5 (the mean particle diameter of 3.8-5.2 micrometers) SHILED EX made from Fuji IRISH-BA Chemistry (mean-particle-diameter [of 3 micrometers], calcium concentration 6 - 8%), SHILED EX SY710 (mean-particle-diameter [of 2.2-2.5 micrometers], calcium concentration 6% - 7.5wt%), etc. can be used calcium concentration 6wt%.

[0058] The phosphate contained in the above-mentioned component (a), (b), and (d) contains the it of all classes, such as simple salt and double salt. Moreover, limitation may not be in the metal cation which constitutes it, and which metal cations, such as phosphoric-acid zinc, magnesium phosphate, calcium phosphate, and aluminum phosphate, are sufficient. Moreover, there is no limitation in whenever [frame / of phosphoric-acid ion / or condensation] etc., any normal salt, 2 hydrogen salt, 1 hydrogen salt, or phosphite are sufficient, and normal salt

contains all condensed phosphates, such as a polyphosphate besides an orthophosphate, further

[0059] Any of a calcium oxide, a calcium hydroxide, and a calcium salt are sufficient as the above-mentioned component (c) and the line compound contained in (d), and these one sort or two sorts or more can be used for it. Moreover, a peach is good using the double salt containing cations other than calcium, such as calcium phosphate and zinc besides the simple salt which especially a limit does not have in the class of calcium salt, either, and contains only calcium as cations, such as a calcium silicate, a calcium carbonate, and calcium phosphate, and calcium phosphate magnesium, and calcium.

[0060] Any of colloidal silica and a dry type silica are sufficient as the silicon oxide contained in the above-mentioned component (b), (c), and (d). As colloidal silica, in using drainage system coat formation resin as the base By the trade name, for example, the Snow tex O by Nissan Chemical Industries, Ltd., Snow tex N The Snow tex 2D, the Snow tex 3D, the Snow tex 4D, the Snow tex C the Snow tex S and a catalyst --- formation --- Industry --- KATARIDOS of make, KATARIDO SI-380, KATARIDO SI-40, and KATARIDO SA --- KATARIDO SN, ADEARITO AT-20-50 by Asahi Denka Kogyo K.K., ADEARITO AT-20N, ADEARITO AT-300, ADEARITO AT-300S, ADEARITOAT200, etc. can be used.

[0061] moreover, in using solvent system coat formation resin as the base By the trade name, for example, ORGANO silica sol MA-ST-M by Nissan Chemical Industries, Ltd. ORGANO silica sol IPA-ST, ORGANO silica sol EG-ST, ORGANO silica sol E-ST-ZL, ORGANO silica sol NPO-ST, ORGANO silica sol DMAC-ST, ORGANO silica sol DMAC-ST-ZL, ORGANO silica sol XBA-ST, ORGANO silica sol MBN-ST, a catalyst --- formation --- Industry --- OSCAL-1132 of make, OSCAL-1232, and OSCAL-1332, OSCAL-1432, OSCAL-1532, OSCAL-1632, OSCAL-1722, etc. can be used.

[0062] Especially an organic solvent distributed silica sol is excellent in dispersibility, and excels fumed silica in corrosion resistance. Moreover, as fumed silica, AEROSIL R871, AEROSIL R812, AEROSIL R811, AEROSIL R874, AEROSIL R202, AEROSILR805 and AEROSIL130 made from Japanese Aerosil, AEROSIL 200, AEROSIL300, AEROSIL 300CF, etc. can be used by the trade name, for example.

[0063] It is thought that a particle silica can control promotion of corrosion by contributing to generation of the corrosion product of precise and stable zinc under corrosive environment, and forming the corrosion product in a plating front face precisely. As for a particle silica, from a corrosion resistance viewpoint, it is desirable that particle diameter uses desirably 5-50nm of 5-20nm of 5-15nm things still more preferably. Limitation does not have molybdate of said component (e) in whenever [frame and condensation], for example, alkylmolybdate, paramolybdate, molybdate, etc. are mentioned. Moreover, as double salt, phosphoric-acid molybdate etc. is mentioned including all salts, such as simple salt and double salt.

[0064] As triazoles, among the organic compounds of the above-mentioned component (f) 1, 2, 4-triazole, 3-amino-1,2,4-triazole, 3-mercapto - 1, 2, 4-triazole, 5-amino-3-mercapto - 1, 2, 4-triazole, 1H-benzotriazole, etc. again as thiols 1,3,5-triazine-2,4,6-trithiol, 2-mercapto Benzimidazole, etc. again as thiazoles 5-amino-2-mercapto - 1, 3, 4-thiadiazole, 2,5-dimercapto-1,3,4-thiadiazole, etc. again as thiazoles 2-N and N-diethylthio benzothiazole and 2-mercaptobenzothiazole are mentioned for a tetrasthythiuram disulfide etc. as thiazams again, respectively.

[0065] the above-mentioned component (a) --- setting --- the compounding ratio of calcium ion-exchange silica (a1) and phosphate (a2) --- the weight ratio of solid content --- (a1) / (a2) = 1 / 99 ~ 99 / 1 --- desirable --- 10 / 90 ~ 90 / 10 --- 20 / 80 ~ 80 / 20 are still more preferably suitable. Less than by 1/99, (a1)/(a2) has few calcium elution volumes, and cannot form only the protective film which blocks a corrosion origin. On the other hand, if 99/1 is exceeded, since phosphoric-acid ion required for formation of a protective film to start the calcium and complexation reaction for the calcium of the amount beyond the need to not only be eluted, but will not be supplied enough, corrosion resistance will fall on the contrary.

[0066] In the above-mentioned component (b) 20 / 80 ~ 80 / 20 are still more preferably suitable, the compounding ratio of calcium ion-exchange silica (b1), phosphate (b2), and silicon oxide (b3)

/1 --- desirable --- 10 / 90 --- 90 / 10 --- (g) --- / (h) = 1 / 99 --- 99 / 1 --- desirable --- 10 / 90 --- 90 / 10 --- 20 / 80 --- 80 / 20 are still more preferably suitable.

381] Here, the effectiveness by (e)/(f) and (e)/(g)+(h) and (f)/(g)+(h) respectively is less than 99 and then different self-repair effectiveness by exceeding 99/1, respectively is not fully required. Moreover, if (g)/(h) has few calcium elution volumes, and cannot form only the protective film which blocks a corrosion origin less than by 1/99 but 99/1 is exceeded on the other hand. Since silicon oxide required for making phosphoric-acid ion and calcium required for the calcium and complexation reaction the calcium of the amount beyond the need not by being eluted, but adsorb for formation of a protective film is not fully supplied, sufficient self-repair effectiveness is not acquired.

382] (e) molybdate of the above (7), (3) triazoles, thiols, in one or more sorts of organic compounds chosen from thiadiazole, thiazoles, and thiarams, and the rust-proofing addition compound which blended (i) calcium ion-exchange silica 20 / 80 --- 80 / 20 are still more preferably suitable, the compounding ratio of these (e), (f), and (i) --- the weight ratio of solid content --- (e)/(f) = 1 / 99 --- 99 / 1 --- desirable --- 10 / 90 --- 90 / 10 --- 20 / 80 --- 80 / 20 are still more preferably suitable, (e) --- / (i) = 1 / 99 --- 99 / 1 --- desirable --- 10 / 90 --- 90 / 10 --- (f) --- / (i) = 99 --- 99 / 1 --- desirable --- 10 / 90 --- 90 / 10 --- 20 / 80 --- 80 / 20 are still more preferably suitable. Here, the effectiveness by (e)/(f) and (e) / (i) and (f) / (i) compounding less than 1/99 and an different self-repair effectiveness by exceeding 99/1, respectively is not fully acquired.

383] Loadings (the above-mentioned component (a) either of (f) of the above-mentioned rust-proofing addition component (B) in the inside of an organic coat. On the loadings of the sum total of the self-repair nature manifestation matter which carried out compound addition of other components to the above (e) and/or (f) the coat formation organic resin (A) 100 weight section (solid content) --- receiving --- the 1 --- 100 weight section (solid content) --- desirable --- 5 --- 80 weight section (solid content) --- it considers as 10 --- 50 weight section (solid content) still more preferably. The corrosion-resistant improvement effectiveness has the small loadings of a rust-proofing addition component (B) in under 1 weight section. On the other hand, if loadings exceed a 100 weight sections, since corrosion resistance will fail, it is not desirable.

384] Into an organic coat, it adds to the above-mentioned rust-proofing addition component mentioned and these one sort or two sorts or more can be used, for example.

385] Into an organic coat, further, if needed, solid lubricant (C) can be blended in order to raise a workability of a coat. As solid lubricant (C) applicable to this invention, the following is mentioned and these one sort or two sorts or more can be used, for example.

386] The Perfluoropolyether, the (2) fluororesin particle, for example, poly fluoro ethylene resin, or polytetrafluoroethylene resin etc., such as polyolefine wax and paraffin wax, for example, ethylene wax, synthetic paraffin, native paraffin, micro wax, and a chlorinated hydrocarbon, vinylidene fluoride resin [0086], etc. moreover --- in addition, a fatty-acid amide system compound (for example, octadecanamide ---) A palmitic-acid amide, methylenebisacetamide, hylene-bis-stearamide, Oleic amide, an ESHRU acid amide, an alkylene screw fatty-acid amide, etc., metal soap (for example, calcium stearate and lead stearate ---) One sort, such as stearic sulfoxide (for example, molybdenum disulfide, tungsten disulfide, etc.), graphite, and apatite fluoride, such as lauric-acid calcium and palmitic-acid calcium, boron nitride, a dialkylene glycol, and an alkali-metal sulfate, or two sorts or more may be used.

387] Also in the above solid lubricant, polyethylene wax and a fluororesin particle (even inside or polytetrafluoroethylene resin particle) are suitable especially, as polyethylene wax --- mentioned by Hoechst A.G. for example 9815A and auction dust 3715 and auction dust 3620 and auction dust 3910 and Mitsubishi --- Formation --- Sun Wachs of make 131-P and Sun Wachs HEMPEARL made from 161-P and Mitsui Petrochemistry W-100 and CHEMPEARL W-200,

CHEMPEARL W-500, and CHEMPEARL W-800 and CHEMPEARL W-950 etc. can be used. [0088] Moreover, as a fluororesin particle, a tetrafluoroethylene particle is the most desirable, for example, it is HUBURON by Daikin Industries, LTD. L-2, RUBURON L-5, Mitsui and 200 by E. I. du Pont de Nemours & Co., Fluon dispersion by Asahi-KCI Fluoropolymers Co., Ltd. AD1, Fluon dispersion AD2, Fluon L141J, Fluon L150J, Fluon L155J etc. are suitable. [MP100 and MP1200] Moreover, the lubrication effectiveness which was excellent with especially concomitant use of a polyolefine wax and a tetrafluoroethylene particle is expectable in these.

388] the loadings of the solid lubricant (C) in the inside of an organic coat --- the coat formation organic resin (A) 100 weight section (solid content) --- receiving --- 1 --- 80 weight section (solid content) --- it considers as 3 --- 40 weight section (solid content) preferably. The lubrication effectiveness is deficient in the loadings of solid lubricant (C) in under 1 weight section, and since paintwork will fail on the other hand if loadings exceed 80 weight sections, it is not desirable.

389] The organic coat which the organic covering steel plate of this invention has is usually the self-repair nature manifestation matter at coat formation organic resin (A), (a) calcium ion-exchange silica and phosphate, (b) calcium ion-exchange silica, phosphate and silicon oxide, the (c) lime compound, and silicon oxide, (d) A lime compound, phosphate and silicon oxide, (e) molybdate, (f) Triazoles, thiols, thiadiazole, and thiazoles one or more sorts of organic compounds chosen from thiarams, and ** --- inner either --- or, although the rust-proofing addition component (B) which carried out compound addition of other components is blended with the above (e) and/or (f) and solid lubricant (C), a curing agent, etc. are added if needed further --- the need --- responding --- as an additive --- an organic color pigment (for example, a condensed multi-ring system organic pigment ---) coloring colors (for example, organic solvent fuelibility azo dye ---), such as a phthalocyanine system organic pigment inorganic pigments, such as a water-soluble azo metal color (for example, titanium oxide etc.), chelating agents (for example, third etc.) and a conductive pigment (for example, zinc ---) Metal powder, such as aluminum and nickel, Lysnized iron, antimony dopes nold tin oxide, etc. can add one sort, such as coupling agents (for example, a silane coupling agent, a titanium coupling agent, etc.) and a melamine cyanuric acid addition product, or two sorts or more.

390] Moreover, the coating constituent containing the above-mentioned coat formation organic resin and an addition component for coat formation usually contains a solvent (an organic solvent and/or water), and a neutralizer etc. is added further if needed. The desiccation thickness of an organic coat sets preferably 0.3-3-micrometer 0.1-5 micrometers to 0.5-2 micrometers still more preferably. The thickness of an organic coat has the insufficient corrosion resistance of less than 0.1 micrometers, and on the other hand, if thickness exceeds 5 micrometers, conductivity and workability will fail.

391] Next, the manufacture approach of the organic covering steel plate of this invention is explained. As opposed to the coat formation organic resin (A) mentioned above after the organic covering steel plate of this invention carried out chemical conversion of the front face of a zinc system plating steel plate or an aluminum system plating steel plate if needed (a) calcium ion-exchange silica and phosphate, (b) calcium ion-exchange silica, phosphate and silicon oxide, the (c) lime compound, and silicon oxide, (d) A lime compound, phosphate and silicon oxide, (e) molybdate, (f) Triazoles, thiols, thiadiazole, and thiazoles one or more sorts of organic compounds chosen from thiarams, and ** --- inner either Or it is manufactured by applying and carrying out stoving of the coating constituent with which the rust-proofing addition component (B) which carried out compound addition of other components was added by the above (e) and/or (f), and solid lubricant (C) etc. was added further if needed. In addition, in order that the front face of a plating steel plate may carry out alkaline-degreasing processing if needed and may raise adhesion and corrosion resistance further before it applies the above-mentioned chemical conversion liquid or a coating constituent, it can pre-treat surface control processing etc.

392] As an approach of coating a plating steel plate front face with chemical conversion liquid, any of a spreading method, an immersion method, and a spray method are sufficient, and which spreading means, such as roll coaters (3 roll methods, 2 roll methods, etc.), a squeeze coating

adine, and a die coating machine, may be used by the spreading method. Moreover, it is also possible to perform adjustment of coverage, equalization of an appearance, and equalization of thickness by the air knife method or the roll extracting method after the spreading processing by squeeze coating machine etc., immersion processing, and spray processing.

[094] Stoving is performed, after coating chemical conversion liquid as mentioned above and using if needed. The approach of carrying out stoving of the coated processing liquid is arbitrary, for example, can use the means of a dryer, an air-heating furnace, a high-frequency-heating furnace, an infrared furnace, etc. As for this stoving processing, it is desirable to perform desirably 80~200-degrees C 40~350 degrees C in 80~160 degrees C still more stoving by attainment board temperature. At less than 40 degrees C, moisture remains so much into a coat and stoving temperature becomes inadequate [corrosion resistance]. On the other hand, if stoving temperature exceeds 350 degrees C, it is not only noneconomic, but it will come easy to produce a defect in a coat, and corrosion resistance will fail.

[095] After forming a chemical conversion coat if needed as mentioned above, the coating constituent for organic coat formation is applied. As an approach of applying a coating constituent, the approach of arbitration, such as the applying method, dip coating, and a spray method, is employable. As an applying method, which approaches, such as roll coaters (3 roll methods, 2 roll methods, etc.), a squeeze coating machine, and a die coating machine, may be used. Moreover, it is also possible to perform adjustment of coverage, equalization of an appearance, and equalization of thickness by the air knife method or the roll extracting method after the spreading processing by a squeeze coating machine etc., immersion processing, or spray processing.

[096] Although stoving is performed after spreading of a coating constituent, without usually using, a rinsing process may be carried out after spreading of a coating constituent. A dryer, an air-heating furnace, a high-frequency-heating furnace, an infrared furnace, etc. can be used for stoving processing. As for heat-treatment, it is desirable to perform 50~350 degrees C 60 degrees C ~ 250 degrees C preferably by attainment board temperature. At less than 50 degrees C, the moisture in a coat remains so much and whenever [stoving temperature] comes inadequate [corrosion resistance]. Moreover, when whenever [stoving temperature] exceeds 350 degrees C, there is a possibility it is not only noneconomic, but that a defect may arise in a coat and corrosion resistance may fail.

[097] This invention contains the steel plate which has a coat which was described above on its sides or one side. Therefore, as a gestalt of this invention steel plate, there is the following, for example.

Example 1: one side: --- a plating coat-chemical conversion coat-organic coat and one sideplating --- a coat (2) one sideplating coat-chemical conversion coat-organic coat and one sideplating coat-chemical conversion coat (3) double-sidedplating coat-chemical conversion coat-organic --- a coat (4) one sideplating coat-chemical conversion coat-organic coat and one sideplating coat-organic coat (5) double-sidedplating coat-organic coat [0058 ---]

Example 2: The solid lubricant shown in the rust-proofing addition component (self-repair nature antistation matter) shown in Table 4 (Table 4-1 and 4-2) and Table 5 was suitably blended with this resin constituent using what is shown in Table 3 as organic resin for organic coat formation, need time amount distribution was carried out using the disperser for coatings (Sandinder), and it considered as the desired coating constituent.

[099] In order to obtain household electric appliances, building materials, and the organic covering steel plate for autoparts, after alkaline-degreasing-processing and rinsing drying the front face of this plating steel plate, using the plating steel plate shown in Table 1 which reformed various zinc system plating or aluminum system plating to cold rolled sheet steel board thickness 0.8mm and surface roughness Ra:1.0micrometer) as a processing negative, chemical conversion was performed on the conditions shown in Table 2 if needed. Subsequently, applied the coating constituent for organic coat formation by the roll coater, it carried out stoving, the organic coat was made to form, and the organic covering steel plate of the example this invention and the example of a comparison was manufactured. The solid content (heating residue) or the spreading conditions of a coating constituent (rolling force of a roll, rotational

speed, etc.) adjusted the thickness of an organic coat.

[0100] About the obtained organic covering steel plate, the quality engine performance (a coat appearance, white-rust-proof, the white-rust-proof after alkaline degreasing, coating adhesion, workability) was evaluated. The result is shown in Table 6 ~ 21 with the coat configuration of a chemical conversion coat and an organic coat etc. Evaluation of the quality engine performance of an organic covering steel plate was performed by [as being the following].

[0101] (1) The homogeneity (existence of nonuniformity) of a coat appearance was evaluated by viewing about coat appearance each sample. The valuation basis is as follows.

Q : the appearance in which the appearance x nonuniformity in which nonuniformity completely twists and uniform appearance **nonuniformity is conspicuous a little is conspicuous [0102] (2) The compound corrosion test (CCT) shown below about white-rust-proof each sample was performed, and the rate of white rust generating area after a predetermined cycle estimated.

[The contents of 1 cycle of a compound corrosion test (CCT)]

3wt% salt spray test (30 degree-C/0.5 hour)

** humidity cabinet test (30 degrees C, 95%RH; 1.5 hours)

** hot-air-drying trial (50 degrees C, 20%RH; 2.0 hours)

** hot-air-drying trial (30 degrees C, 20%RH; 2.0 hours)

The valuation basis is as follows.

O O [-white-rust-generating-less] : Less than [5% of rates of white rust generating area] O : 5% or more of rates of white-rust generating area, 10% or more of rates of less than 10%O- white-rust area, less-than [25%] ** : 25% or more of rates of white rust generating area, less than [50%] x : 50% or more of rates of white rust generating area [0103] (3) After performing alkaline degreasing by alkali treatment liquid CLN-384S (50 degrees C, spray 2 minutes) by Nihon Parkerizing Co., Ltd. the above-mentioned compound corrosion test (CCT) was performed, and the rate of white rust area after a predetermined cycle estimated white-rust-proof each sample after alkaline degreasing. The valuation basis is as follows.

O O [-white-rust-generating-less] : Less than [5% of rates of white rust generating area] O : 5% or more of rates of white-rust generating area, 10% or more of rates of less than 10%O- white-rust generating area, less-than [25%] ** : 25% or more of rates of white rust generating area, less than [50%] x : 50% or more of rates of white rust generating area [0104] (4) After painting the baking paint (30 micrometers of thickness) of a melamine system, it was immersed into priming for 2 hours, the cut of the squares (it is the squares of 10x10 at intervals of 1mm) was put in immediately, attachment and exfoliation by adhesive tape were performed, and the stripped plane moment of a paint film estimated coating adhesion each sample. The valuation basis is as follows.

O 5% or more of less than 5% [of -exfoliation-less O-stripped plane moments] **stripped plane moments, less than [20%] x : 20% or more of stripped plane moments [0105] (5) Deep-drawing shaping (iron-oiling conditions) was performed by diameter prior workability blank 20mm, and diameter prior dice50mm, and shaping height until a crack arises estimated. The valuation basis is as follows.

O .diaphragm omission O-height [shaping / of 30mm or more] **shaping height of 20mm or more, less than [30mm] x : shaping height of less than 20mm [0106]

Table 1

項目	単位	評価基準 (g/m ²)
1. 塩化亜鉛の含有率		20
2. 硫酸亜鉛の含有率		60
3. 全亜鉛の含有率 (質量%)		60
4. 亜鉛 (Zn) の含有率 (質量%)		90
5. 亜鉛 (Zn) の含有率 (質量%)		90
6. 亜鉛 (Zn) の含有率 (質量%)		90

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外装	仕 様				区 分
	部白錆付 CCT	部の部白錆付 CCT	部の部白錆付 CCT	部の部白錆付 CCT	
40	○	○	○	○	比 較 例
41	○	○	○	○	比 較 例
42	○	○	○	○	比 較 例
43	○	○	○	○	比 較 例
44	○	○	○	○	比 較 例
45	○	○	○	○	比 較 例
46	○	○	○	○	比 較 例
47	○	○	○	○	比 較 例
48	○	○	○	○	比 較 例
49	○	○	○	○	比 較 例

1 部白錆付不可

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外装	第一層被膜				区分	
	部白錆付 CCT	部の部白錆付 CCT	部の部白錆付 CCT	部の部白錆付 CCT		
40	○	○	○	○	比較例	
41	○	○	○	○	比較例	
42	○	○	○	○	比較例	
43	○	○	○	○	比較例	
44	○	○	○	○	比較例	
45	○	○	○	○	比較例	
46	○	○	○	○	比較例	
47	○	○	○	○	比較例	
48	○	○	○	○	比較例	
49	○	○	○	○	比較例	

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品 名	仕 様				区 分
	部白錆付 CCT	部の部白錆付 CCT	部の部白錆付 CCT	部の部白錆付 CCT	
40	○	○	○	○	比 較 例
41	○	○	○	○	比 較 例
42	○	○	○	○	比 較 例
43	○	○	○	○	比 較 例
44	○	○	○	○	比 較 例
45	○	○	○	○	比 較 例
46	○	○	○	○	比 較 例
47	○	○	○	○	比 較 例
48	○	○	○	○	比 較 例
49	○	○	○	○	比 較 例

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品 種	第一場決選				第二場決選						区 分	
	部白錆付 CCT	部白錆付 CCT	部白錆付 CCT	部白錆付 CCT	結構特性配合		部白錆付 CCT		部白錆付 CCT	部白錆付 CCT		
					部白錆付 CCT	部白錆付 CCT	部白錆付 CCT	部白錆付 CCT				
50	1	1	1	1	1	1	1	1	1	1	1	1
51	1	1	1	1	1	1	1	1	1	1	1	1
52	1	1	1	1	1	1	1	1	1	1	1	1
53	1	1	1	1	1	1	1	1	1	1	1	1
54	1	1	1	1	1	1	1	1	1	1	1	1
55	1	1	1	1	1	1	1	1	1	1	1	1
56	1	1	1	1	1	1	1	1	1	1	1	1
57	1	1	1	1	1	1	1	1	1	1	1	1
58	1	1	1	1	1	1	1	1	1	1	1	1
59	1	1	1	1	1	1	1	1	1	1	1	1
60	1	1	1	1	1	1	1	1	1	1	1	1
61	1	1	1	1	1	1	1	1	1	1	1	1
62	1	1	1	1	1	1	1	1	1	1	1	1
63	1	1	1	1	1	1	1	1	1	1	1	1

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外 観	特 徴			区 分
	前記特徴 CCT	後記特徴 CCT	製造方法	
①	○	○	①	本発明例
②	○	○	②	本発明例
③	○	○	③	本発明例
④	○	○	④	本発明例
⑤	○	○	⑤	本発明例
⑥	○	○	⑥	本発明例
⑦	○	○	⑦	本発明例
⑧	○	○	⑧	本発明例
⑨	○	○	⑨	本発明例
⑩	○	○	⑩	本発明例
⑪	○	○	⑪	本発明例
⑫	○	○	⑫	本発明例
⑬	○	○	⑬	本発明例
⑭	○	○	⑭	本発明例
⑮	○	○	⑮	本発明例
⑯	○	○	⑯	本発明例
⑰	○	○	⑰	本発明例
⑱	○	○	⑱	本発明例
⑲	○	○	⑲	本発明例
⑳	○	○	⑳	本発明例
㉑	○	○	㉑	本発明例
㉒	○	○	㉒	本発明例
㉓	○	○	㉓	本発明例
㉔	○	○	㉔	本発明例
㉕	○	○	㉕	本発明例
㉖	○	○	㉖	本発明例
㉗	○	○	㉗	本発明例
㉘	○	○	㉘	本発明例
㉙	○	○	㉙	本発明例
㉚	○	○	㉚	本発明例
㉛	○	○	㉛	本発明例
㉜	○	○	㉜	本発明例
㉝	○	○	㉝	本発明例
㉞	○	○	㉞	本発明例
㉟	○	○	㉟	本発明例
㊱	○	○	㊱	本発明例
㊲	○	○	㊲	本発明例
㊳	○	○	㊳	本発明例
㊴	○	○	㊴	本発明例
㊵	○	○	㊵	本発明例
㊶	○	○	㊶	本発明例
㊷	○	○	㊷	本発明例
㊸	○	○	㊸	本発明例
㊹	○	○	㊹	本発明例
㊺	○	○	㊺	本発明例
㊻	○	○	㊻	本発明例
㊼	○	○	㊼	本発明例
㊽	○	○	㊽	本発明例
㊾	○	○	㊾	本発明例
㊿	○	○	㊿	本発明例

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able 16]

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外 観	特 徴			区 分
	前記特徴 CCT	後記特徴 CCT	製造方法	
①	○	○	①	本発明例
②	○	○	②	本発明例
③	○	○	③	本発明例
④	○	○	④	本発明例
⑤	○	○	⑤	本発明例
⑥	○	○	⑥	本発明例
⑦	○	○	⑦	本発明例
⑧	○	○	⑧	本発明例
⑨	○	○	⑨	本発明例
⑩	○	○	⑩	本発明例
⑪	○	○	⑪	本発明例
⑫	○	○	⑫	本発明例
⑬	○	○	⑬	本発明例
⑭	○	○	⑭	本発明例
⑮	○	○	⑮	本発明例
⑯	○	○	⑯	本発明例
⑰	○	○	⑰	本発明例
⑱	○	○	⑱	本発明例
⑲	○	○	⑲	本発明例
⑳	○	○	⑳	本発明例
㉑	○	○	㉑	本発明例
㉒	○	○	㉒	本発明例
㉓	○	○	㉓	本発明例
㉔	○	○	㉔	本発明例
㉕	○	○	㉕	本発明例
㉖	○	○	㉖	本発明例
㉗	○	○	㉗	本発明例
㉘	○	○	㉘	本発明例
㉙	○	○	㉙	本発明例
㉚	○	○	㉚	本発明例
㉛	○	○	㉛	本発明例
㉜	○	○	㉜	本発明例
㉝	○	○	㉝	本発明例
㉞	○	○	㉞	本発明例
㉟	○	○	㉟	本発明例
㊱	○	○	㊱	本発明例
㊲	○	○	㊲	本発明例
㊳	○	○	㊳	本発明例
㊴	○	○	㊴	本発明例
㊵	○	○	㊵	本発明例
㊶	○	○	㊶	本発明例
㊷	○	○	㊷	本発明例
㊸	○	○	㊸	本発明例
㊹	○	○	㊹	本発明例
㊺	○	○	㊺	本発明例
㊻	○	○	㊻	本発明例
㊼	○	○	㊼	本発明例
㊽	○	○	㊽	本発明例
㊾	○	○	㊾	本発明例
㊿	○	○	㊿	本発明例

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able 17]

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[illegible]

[Translation done.]

126] able 20}

試料名	第一精製液			第二精製液					成分	
	系	類	濃度 (mg/ml)	組成物	陽極液成分 (%)		陽極液成分 ($^{\circ}\text{C}$)			電極 位置
					陽極	陰極	陽極	陰極		
41	+	+	+	+	+	+	+	+	+	
42	+	+	+	+	+	+	+	+	+	
43	+	+	+	+	+	+	+	+	+	
44	+	+	+	+	+	+	+	+	+	
45	+	+	+	+	+	+	+	+	+	
46	+	+	+	+	+	+	+	+	+	
47	+	+	+	+	+	+	+	+	+	
48	+	+	+	+	+	+	+	+	+	
49	+	+	+	+	+	+	+	+	+	
50	+	+	+	+	+	+	+	+	+	
51	+	+	+	+	+	+	+	+	+	
52	+	+	+	+	+	+	+	+	+	
53	+	+	+	+	+	+	+	+	+	
54	+	+	+	+	+	+	+	+	+	
55	+	+	+	+	+	+	+	+	+	
56	+	+	+	+	+	+	+	+	+	
57	+	+	+	+	+	+	+	+	+	
58	+	+	+	+	+	+	+	+	+	
59	+	+	+	+	+	+	+	+	+	
60	+	+	+	+	+	+	+	+	+	
61	+	+	+	+	+	+	+	+	+	
62	+	+	+	+	+	+	+	+	+	
63	+	+	+	+	+	+	+	+	+	
64	+	+	+	+	+	+	+	+	+	
65	+	+	+	+	+	+	+	+	+	
66	+	+	+	+	+	+	+	+	+	
67	+	+	+	+	+	+	+	+	+	
68	+	+	+	+	+	+	+	+	+	
69	+	+	+	+	+	+	+	+	+	
70	+	+	+	+	+	+	+	+	+	
71	+	+	+	+	+	+	+	+	+	
72	+	+	+	+	+	+	+	+	+	
73	+	+	+	+	+	+	+	+	+	
74	+	+	+	+	+	+	+	+	+	
75	+	+	+	+	+	+	+	+	+	
76	+	+	+	+	+	+	+	+	+	
77	+	+	+	+	+	+	+	+	+	
78	+	+	+	+	+	+	+	+	+	
79	+	+	+	+	+	+	+	+	+	
80	+	+	+	+	+	+	+	+	+	
81	+	+	+	+	+	+	+	+	+	
82	+	+	+	+	+	+	+	+	+	
83	+	+	+	+	+	+	+	+	+	
84	+	+	+	+	+	+	+	+	+	
85	+	+	+	+	+	+	+	+	+	
86	+	+	+	+	+	+	+	+	+	
87	+	+	+	+	+	+	+	+	+	
88	+	+	+	+	+	+	+	+	+	
89	+	+	+	+	+	+	+	+	+	
90	+	+	+	+	+	+	+	+	+	
91	+	+	+	+	+	+	+	+	+	
92	+	+	+	+	+	+	+	+	+	
93	+	+	+	+	+	+	+	+	+	
94	+	+	+	+	+	+	+	+	+	
95	+	+	+	+	+	+	+	+	+	
96	+	+	+	+	+	+	+	+	+	
97	+	+	+	+	+	+	+	+	+	
98	+	+	+	+	+	+	+	+	+	
99	+	+	+	+	+	+	+	+	+	
100	+	+	+	+	+	+	+	+	+	

127] 2518 213

[illegible]

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effect of the invention.] As stated above, moreover, the organic covering steel plate of this invention has corrosion resistance advanced as an organic covering steel plate of the application building materials, household electric appliances, an automobile, etc. in the coat component of a processing liquid at the time of manufacture, or a product, excluding hexavalent chromium at and is excellent in a coat appearance, coating adhesion, etc.